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MODERN COLLOIDS

An Introduction to the Physical Chemistry of Large Molecules and Small Particles

BY

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1948

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Dedicated to

THOSE MEN WHO HAVE RAISED
COLLOIDS TO THE DIGNITY
OF AN EXACT SCIENCE

PREFACE

This book is designed to serve as an introduction to the behavior of colloidal materials. It is based on a course for undergraduate students who intend to specialize in chemistry, biology, medicine or agriculture. In many schools colloid chemistry, if it is given at all, is reserved for graduate students, and the average undergraduate may justly complain that chemistry does not tell very much about the things he sees outside the classroom.

There is general agreement that colloid chemistry is valuable for students of the biological sciences. That it is indispensable for students who contemplate a career in industrial chemistry is less widely recognized. The fact that virtually all chemical products are either colloidal or are purified or otherwise treated by colloidal materials is sufficient justification for the inclusion of colloids in the chemistry curriculum.

Colloid chemistry has made great strides in the past ten or fifteen years, which may be said to mark the coming of age of the science. It has also given rise to at least one lusty offshoot, lpoymer science, which is already a respectable science in its own right: so respectable in fact that some polymer chemists refuse to admit that they deal with colloids. This attitude undoubtedly reflects the bad repute into which colloid chemistry had fallen. Colloids was once a synonym for complex terminology and unpredictable behavior. Although it is still necessarily complex we are beginning to see our way clearly and much of the dead wood is being cleared away.

The recent advances in colloid chemistry stem from several sources. Primary among these is the realization that atoms are not merely symbols or points but have definite sizes and shapes. For this concept chemistry is indebted to physics, especially to the two Braggs, for their interpretation of X-ray diffraction patterns, and to the theoretical chemists whose work is well exemplified in the publications of Linus Pauling.

From the organic chemists came the concept of a high polymer as a single molecule. This idea, although not new, was first employed successfully by Carothers in this country and by Staudinger, Meyer and Mark in Europe. Although of primary value in the field of synthetic plastics and rubbers, the high polymer concept has also made possible a logical interpretation of the behavior of such natural products as proteins, cellulose, starches and gums as well as of some minerals.

Physical chemistry has contributed to colloids a realization of the necessity for making exact measurements on pure systems. An outstanding example of the power of this approach is shown by the development of our knowledge of soaps and related detergents, as reflected in the publications of J. W. McBain and his collaborators.

Perhaps nowhere in science has the progress of a particular field been aided so much by the development of new tools. We need mention only the electron microscope, the ultracentrifuge, and of course the X-ray diffraction camera at this time.

Whether this book presents an adequate survey of colloid chemistry must be determined by the reader. It is not intended to be exhaustive, although it is believed that the references at the end of each chapter will serve as an adequate introduction to the various specialized subdivisions.

Footnote references to original papers have been used sparingly. Most of the mathematical development has been set in smaller type together with some material of a theoretical nature. The material in this book can, with careful cutting, be fitted into a one semester course, although a full year would be more nearly adequate to cover the subject.

This book may also be useful for refresher courses or as a desk-reference for chemists who wish to keep up with the trends in modern chemistry.

R. B. D.

University of Hawaii
September, 1947

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This book would not have been possible without the unflagging aid of my wife who typed the manuscript and helped to correct proofs and prepare the index.

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CHAPTER I

INTRODUCTION

Field of Colloids.—Nearly everything we see is colloidal. The common molecules of inorganic chemistry and the common small molecules of organic chemistry are molecules of substances which are rarely encountered in a pure state in everyday life. When you get up in the morning you wash with colloidal soap, put on your colloidal clothes, read a colloidal newspaper while eating a colloidal breakfast. The house you live in and the pavement you walk on are both colloidal; even you yourself consist entirely of colloidal materials. The mineral kingdom is partly colloidal, the vegetable and animal kingdoms wholly so. Colloid science is the link joining chemistry to all the biological sciences. It is also the most frequently encountered branch of applied chemistry in industrial practice.

Colloid materials enter into almost every branch of chemistry. If you look at the current issue of "Chemical Abstracts," you will find that all but one of its thirty-one departments are likely to contain articles on colloids. Even "Subatomic Phenomena and Radiochemistry" contains abstracts of X-ray investigations of colloids.

The wide scope of colloid science is shown in the following selection of applications, which could be extended even further.

Some Applications of Colloid Chemistry

1. Agriculture:	Agricultural science deals with soil colloids and colloidal crops.
2. Biology and medicine:	All biological systems are colloidal.
3. Analytical chemistry:	The coagulation of precipitates and the adsorption of impurities are colloidal phenomena.
4. Organic chemistry:	The behavior of high polymeric "plastics" is colloidal, as are the tars formed in organic synthesis.
5. Industrial processes:	Certain industrial processes, especially those of purification, are colloidal. Examples are the purification of water, sugar, fats, solvents, air, and the disposal of sewage.

6. Industrial products:	Some colloidal industrial products include plastics, rubber, detergents, paints, fabrics, paper, cement, ceramics, cosmetics, food.

There is hardly a single industry that does not at some stage have to take into account at least one aspect of colloidal behavior.

It is not lack of importance that has prevented colloid science from assuming a more prominent role among her sister sciences. Practical importance is often irrelevant in pure science. There is one thing only that can prevent a body of information from being classified as a science, and that is lack of precision. This fault does not always lie with the men who make the observations; it may be inherent in the subject. Subjects such as the social sciences, where the number of uncontrollable variables so greatly exceed the number of possible observations, can never hope to be precise no matter how great the genius of the observer. Frequently, however, greater precision in observation is possible. Many investigations in the field of colloid science have been made on impure materials whose composition is not precisely known. In every case, if those observations are to be of wider application, they must be repeated on material of known composition. Chemistry deals with the behavior of pure substances and colloid science must do likewise if it is to progress.

What Is Colloid Science?—Before attempting to define colloid science it will be well to examine some of the subjects which are dealt with in related branches of study. The study of mechanics and hydraulics deals with the behavior of objects in bulk and does not need to take cognizance of the structure of the materials. Newton's laws of motion apply equally well to an apple and to the moon. The flow of water in a pipe can be explained without any knowledge of the structure or composition of water molecules. A large part of the study of chemistry deals with the behavior of molecules. A single molecule is too small to work with but we are fortunate in being able to prepare reasonably pure substances in which all the molecules are identical. The chemical reaction of zinc with hydrochloric acid is quite independent of the size of the piece of zinc or the quantity of acid. The concentration of the acid is, of course, important in controlling the rate of the reaction, but the end products are the same regardless of the shape of the zinc or the size of the vessel.

Colloid chemistry deals with particles which are so small that they behave in some respects like molecules, and with molecules so large that they behave in some respects like particles. It is possible to consider colloids as very finely divided matter or as very large molecules. The second point of view has been the more successful, especially in recent years, because it enables us to build upon the established facts of chemistry. This book represents an attempt to present a number of important colloidal phenomena in terms of the forces which exist between atoms. The success of this attempt must be judged by the extent to which it makes intelligible a large body of apparently unrelated facts.

For many years the description of the behavior of small particles was left outside the folds of conventional physics and chemistry. Colloidal gold, for example, does not behave like a mixture of sand and water, which can be described by mechanics; nor does it behave like a solution of sugar, which can be described by chemistry. In some respects it is like the former and in some like the latter. It is also true that in some ways it is unlike the former, and in some unlike the latter. Such unconventional behavior is frequently punished by neglect. Physics made great advances in the seventeenth century under the leadership of Newton, and chemistry made its great advance in the eighteenth century under the leadership of Lavoisier; but it was not until the nineteenth century that the behavior of matter in the colloidal range of subdivision was observed and described, and it is only in the present century that our knowledge of the behavior of molecules and atoms has become sufficiently complete to enable us to extend it to the field of colloid science.

The Size and Shape of Colloidal Materials.—When dealing with very small dimensions it is convenient to define units in such a way that it is not necessary to introduce infinitesimally small, hence unfamiliar, numbers. Table 1–1 contains the definitions of customary units of length. It is not at this stage necessary to define any units smaller than 10^{-8} cm (1 Ångstrom unit = 1 Å), for diameters of atoms

TABLE 1–1. METRIC UNITS OF LENGTH

Name	Symbol	Equivalent
Meter	m	1 m = 10^2 cm
Centimeter	cm	1 cm = 1 cm = 10^8 Å
Millimeter	mm	1 mm = 10^{-1} cm = 10^7 Å
Micron	μ	1μ = 10^{-4} cm = 10,000 Å
Millimicron	mμ*	1mμ = 10^{-7} = 10 Å
Ångstrom unit	Å	1 Å = 10^{-8} cm

* The millimicron is sometimes written $\mu\mu$.

are all larger than this. Dimensions smaller than the diameter of an atom are rarely met except in the study of atomic nuclei.

Atoms have diameters of about 2 to 3 Å the diameters of the common inorganic molecules are about 7 to 10 Å; the lengths of the common organic molecules are rarely greater than 20 Å. This value of 20 Å is of some interest. It happens to be about the best resolution yet achieved by the most recent type of electron microscope. We can conveniently consider particles whose diameters are greater than 20 Å as colloidal particles. A spherical particle with this diameter having the same density as water would have a molecular weight of nearly 3000.

The volume of a sphere is $1/6\pi d^3$, so the volume of a sphere 20 Å in diameter will be:

$$1/6\pi \times (20 \times 10^{-8})^3 \qquad \text{or} \qquad 4.2 \times 10^{-21}\ \text{cm}^3.$$

The weight of this sphere, if it has unit density, will be 4.2×10^{-21} gm. The molecular weight of any substance is the weight of one mol or Avogadro's number of molecules. Avogadro's number is 6.023×10^{23}, so the molecular weight of the sphere will be: $6.023 \times 10^{23} \times 4.2 \times 10^{-21}$ which equals about 2.5×10^3 or 2500.

Let us now examine the upper limit of particle size. We see objects by means of ordinary light of wave lengths between 4000 to 7500 Å. Even the best optical microscope is limited in its resolving power by the wave length of the light used for illumination. Consequently particles smaller than about 1000 Å in diameter are submicroscopic (but not sub-electron-microscopic. See page 16). It is probable that the type of behavior in which we are interested, and which we will learn to call colloidal, is shown not only by particles in the range of sizes from 20 Å to 1000 Å, but also by particles even larger than 1000 Å in diameter. No system of classification can impose rigid bounds on its subdivisions, for nature is oblivious of our desires to put her phenomena away in neatly defined pigeonholes. This range of particle sizes, therefore, must be kept in mind merely as an approximate index and not as an exclusive principle.

One should not lose sight of the fact that the natural laws which describe the behavior of matter in the molecular or the massive state also apply to the colloidal state. Some of these laws may not be prominently operative, whereas others less noticeable in the other states may come into more prominence in the colloidal state. The degree of subdivision imposes certain conditions on the behavior of a colloid system, but it does not alter the laws of chemistry and mechanics which govern its behavior.

If you divide something into smaller and smaller parts, the total surface area increases as the particle size decreases. It is relatively easy to show that the surface area of a collection of cubes is six times the volume divided by the length of one side. The volume of a cube is d^3 if d is the length of one side. The area of one face is d^2 and as there are 6 faces the total area is $6d^2$. The area, A, is therefore equal to six times the volume divided by the length of one side,

$$A = 6d^3/d = 6V/d. \tag{1-1}$$

The area of a collection of similar cubes is n times the area of one cube if n is the number of cubes. The total volume is also nV; thus equation 1–1 applies equally well to a single cube and to a collection of similar cubes.

The same equation applies to a sphere or a collection of spheres if D is the diameter. The area of a sphere is $4\pi r^2$ and the volume is $4/3\pi r^3$. The ratio of the area to the volume is, therefore,

$$A/V = 4\pi r^2/(4/3\pi r^3) = 3/r. \tag{1-2}$$

The radius, r, equals $d/2$, so we can write,

$$A/V = 6/d. \tag{1-3}$$

Therefore,

$$A = 6V/d. \tag{1-1}$$

A calculation will reveal the magnitude of the surface areas involved. One milligram of a solid material, with a density of 1 gm per cm³, is divided into spherical particles 100 Å in diameter. The total surface area may be calculated as follows. Since the density is 1 gm per cc, the volume of 1 mg of material is 10^{-3} cc. To keep the units consistent it is necessary to change from Ångstrom units, in which diameter is expressed, to centimeters. From Table 1–1 it can be seen that 100 Å = 10^{-6} cm. From equation 1–1, therefore,

$$A = 6 \times 10^{-3}/10^{-6} = 6 \times 10^3 = 6000 \text{ cm}^2.$$

It is not uncommon for colloidal particles to have surface areas even larger than 6000 cm² per mg. The figure 10,000 cm² per mg is often seen for certain organic colloids. The surfaces of very porous materials approach similar values. Surfaces have physical and chemical properties which differ, sometimes markedly, from the properties of the interior. Since small colloidal particles have such a large surface area, it is not surprising that the physics and chemistry of surfaces are an intimate part of colloid science.

Definitions.—The boundaries of an important field of study can rarely be defined exactly. As we study any subject we should expect to discover new facts which may render our *a priori* definitions obsolete. Definitions which divide up the realm of natural phenomena should be used as guide posts rather than as boundary markers. We can say that a colloidal system exists wherever an appreciable fraction of the molecules lies at a surface. In practice this will be true in systems which contain particles or pores whose diameters lie in the range 40 Å to 1000 Å. Systems having large extensions in one or two dimensions (fibers or films) will exhibit colloidal phenomena when as thin as 10 Å, even though they may extend for 50,000 Å in another dimension. Systems containing very large molecules, such as the natural and synthetic plastics, fibers, and rubbers, behave as colloids not only when dispersed but also in the pure state. In some cases the molecules are so large that they are frequently held to be continuous throughout the particles.

Thomas Graham derived the name "colloid" from the Greek word for glue (or gelatine). He defined a colloidal suspension as one which could not diffuse through the fine pores of vegetable parchment.[1]

The name "colloid" was thus derived from a representative member of the great class of stable or lyophilic (Greek = liquid-loving) colloids. This book deals first with methods for examining colloids and with the properties of surfaces, and then with the stable colloids from the point of view of their molecular structure. Most of the substances of this class are very large molecules which we call high polymers. The high polymers include all the synthetic plastics and rubbers, all fibers and their derivatives, such as Cellophane, and all protein substances including partially hydrolyzed proteins such as gelatine or glue.

After a discussion of organic high polymers and of colloidal ions, we deal with the inorganic high polymers which include silica gel, clay, and hydrous oxides. The final chapter is reserved for the lyophobic or metastable colloids such as colloidal gold and colloidal sulfur. This branch of colloid science is probably the most difficult to deal with because the systems are very unstable. Nearly all of the properties of the lyophobic colloids depend upon the presence of impurities and many of the classical experiments of colloid chemistry cannot be repeated because modern chemicals do not contain the impurities which were present in the original reagents.

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[1] Alexander, Jerome, *Colloid Chemistry—Principles and Applications*, 4th Ed., p. 3–5 (1937).

Types of Colloids.—The existence of a surface is possible only at the interface between two phases or states of matter. There are three states of matter—gas, liquid and solid—and combining them two at a time produces nine possible systems. A mixture of gases, however, is always a single gaseous phase, so one of the nine systems has to be excluded from our list of colloidal disperse systems.

Types of Heterogeneous Dispersion

	Dispersed Phase	*Continuous Phase*	*Examples of Colloid Systems*
1.	Gas	Liquid	Foam.
2.	Gas	Solid	Solid foam such as pumice or porous solid such as charcoal.
3.	Liquid	Gas	Mist, fog.
4.	Liquid	Liquid	Emulsions, such as milk.
5.	Liquid	Solid	Some emulsions approach this condition, such as mayonnaise; also charcoal in water.
6.	Solid	Gas	Smokes and dust.
7.	Solid	Liquid	Colloidal suspensions. Most colloidal systems are of this type.
8.	Solid	Solid	These are usually derived from the solid in liquid type, for example many colored glasses and precious stones.

This list of disperse colloidal systems has in every case the phases divided into continuous and dispersed. It is not always necessary to have one of the phases dispersed in the other. When one continuous phase is solid, the other phase may also be continuous, just as two continuous nets of different yarns may be interwoven. Highly porous solids, such as silica gel or charcoal, are examples of colloids consisting of a solid and a gaseous phase both of which are continuous. The same substances filled with water would represent systems containing continuous solid and liquid phases.

The size of the dispersed phase of emulsions and foams is almost always greater than 1000 Å and foams may consist of bubbles 1 cm in diameter or even larger. Although the bubbles and drops of foams and emulsions are not of colloidal dimensions, these systems are classed as colloid, because they always contain a third component in the interface. This third component is the stabilizing agent and it is ordinarily a colloidal material.

Sources of Published Information.—Sooner or later a student of colloid science will require more information than is supplied in this book. More advanced discussion of colloids is to be found in several general texts, such as those in the following list which are arranged in inverse chronological order.

General Texts on Colloid Science

1. A. G. Ward, *Colloids, Their Properties and Applications,* Interscience Publishers, New York (1945).
2. W. K. Lewis, L. Squires and G. Broughton, *Industrial Chemistry of Colloidal and Amorphous Materials,* Macmillan, New York (1943).
3. H. B. Weiser, *Colloid Chemistry,* Wiley, New York (1939).
4. J. R. Hartman, *Colloid Chemistry,* Houghton Mifflin, New York (1939).
5. E. A. Hauser, *Colloidal Phenomena,* McGraw-Hill, New York (1939).
6. R. A. Gortner, *Outlines of Biochemistry,* pp. 1–350. Wiley, New York (1938).
7. Jerome Alexander, *Colloid Chemistry: Principles and Applications,*[2] D. Van Nostrand, New York (1937).
8. T. Svedberg, *Colloid Chemistry,* The Chemical Catalog Co. (now Reinhold), New York (1928).
9. H. Freundlich, *Colloid and Capillary Chemistry,* Methuen, London (1926).

In addition to general texts there are monographs on special subjects. The end of each chapter of this book contains a list of references from which more information on the subject matter may be obtained. You should cultivate the habit of referring to these and other books as well as to original references for confirmation, clarification, and amplification of any aspect of colloidal chemistry that arouses your interest.

The literature dealing with colloid science is especially rich in the number of collected articles and symposia. The more useful of these are contained in the following list.

Symposia and Collections

1. *Advances in Colloid Science,* Vols. 1 and 2, Interscience Publishers, New York (1942–46).
2. Jerome Alexander (Ed.), *Colloid Chemistry: Theoretical and Applied,* Vols. 1–6, Reinhold, New York (1926–1946).
   Abbreviated to *Alexander's Colloid Chemistry.*

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[2] Not to be confused with *Alexander's Colloid Chemistry: Theoretical and Applied,* a six-volume collection of papers by specialists.

3. *Colloid Symposium Monographs*, Vol. 1- (1924-). Wiley, New York. (Recent symposia have been published as a part of the Journal of Physical Chemistry.)
4. *High Polymers*, a Series of Monographs on the Chemistry, Physics and Technology of High Polymeric Substances. Vol. 1–7, Interscience Publishers, New York (1940–1946).
5. R. H. Bogue (Ed.), *The Theory and Application of Colloidal Behavior*, 2 Vols., McGraw-Hill, New York (1924).

The most detailed accounts of specialized topics in colloid science are to be found in various scientific and technical journals. A list of the journals in which articles of interest to students of colloids may be found is appended.

✓ SCIENTIFIC AND TECHNICAL JOURNALS IN WHICH ARTICLES ON COLLOID SCIENCE MAY BE PRINTED

Journal of Colloid Science (U.S.A.) (Organized in 1946).
Journal of Polymer Science (U.S.A.) (Organized in 1946).
Journal of the American Chemical Society.
Journal of the Chemical Society (London).
Proceedings of the Royal Society (London).
Philosophical Transactions of the Royal Society (London).
Transactions of the Faraday Society (London).
Journal of Physical Chemistry (U.S.A.).
Comptes Rendus hebdomadaires des Séances de l'Académie des Sciences (Paris).
Journal of Physical Chemistry (U.S.S.R.) (Summaries in English, French, or German).
Journal of Chemical Physics (U.S.A.).
Kolloid Zeitschrift (full title: Zeitschrift für Chemie und Industrie der Kolloide) (German).
Kolloidchemiche Beihefte (later Kolloid-Beihefte) (German).
Zeitschrift für physikalische Chemie (German).
Oil and Soap (U.S.A.).
Soil Science (U.S.A.). ✓

The most complete guide to the printed literature on chemistry and physics throughout the world is Chemical Abstracts. No one section of Chemical Abstracts is reserved by specific title for colloid science, probably because the subject is ubiquitous. But every paper of interest to the student of colloids is abstracted somewhere inside its bulky volumes. Without indexes it would be impossible to use Chemical Abstracts; therefore, extraordinarily detailed indexes are provided every year. These are collected and re-issued at intervals of ten years, in the impressive and valuable Decennial Indexes. The existence of Chemical Abstracts and its indexes makes it possible for students to search the printed literature with some hope of reasonable thoroughness.

Chemical Abstracts was started in 1907. For earlier references the German journal *Chemisches Zentralblatt* provides abstracts back to 1830, and the British *Journal of the Chemical Society* provides them back to 1849.

CHAPTER 2

METHODS FOR DETERMINING THE SIZE AND SHAPE OF COLLOIDAL PARTICLES

Light Microscopes.—One of our basic definitions of a colloidal particle is that it has one dimension which is less than 1000 Å. In order that this definition be useful, it is necessary to be able to determine, with some degree of accuracy, the size of a particle. When we want to examine an object which is too small to see conveniently, we magnify it. A hand-lens can give useful magnification up to about 20 diameters. This means that a line 1 mm long will appear to be 20 mm long when viewed through the lens. Some photographic enlargers will also produce a magnification of about 20 fold.

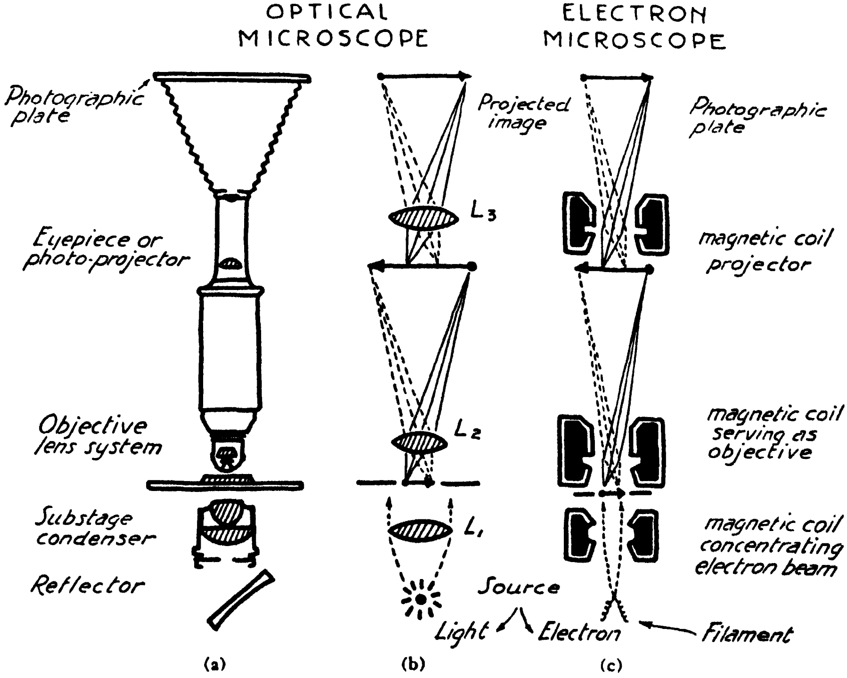

FIG. 2–1. Comparison of light microscope and magnetic electron microscope. (From Burton and Kohl, *The Electron Microscope*, Reinhold (1942).

To get greater magnification it is necessary to use a compound microscope. Figure 2–1b illustrates the essential parts of a compound microscope. The object is illuminated from below by a condensing lens. A magnified image of the object is formed by the objective lens and this image is further magnified by the eyepiece lens. Both objective and eyepiece lenses are usually compound lenses to reduce aberrations, but each compound lens could theoretically be replaced by an equivalent single lens. Compound microscopes provide visual magnification up to about 1000 times; thus a particle 1μ long appears to be 1 mm long. The image produced by a compound microscope can be magnified by additional lenses but this further magnification does not show any more detail than can be seen in the microscope directly. To understand why a microscope cannot give a useful magnification much greater than 1000 times we must first consider the structure of light rays.

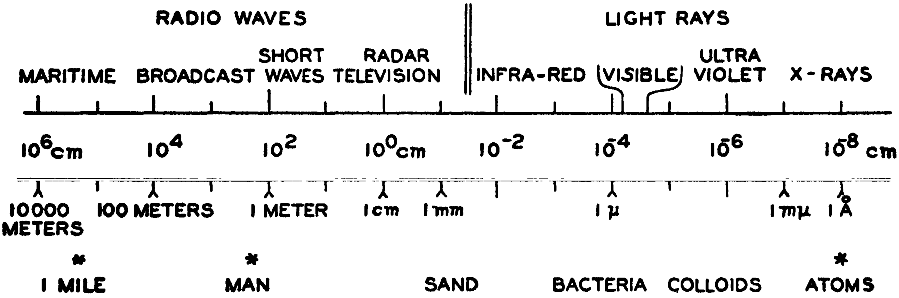

Fig. 2–2. Logarithmic scale of lengths.

Light behaves as if it consisted of trains of transverse waves moving with a velocity of 3×10^{10} cm per sec in a vacuum and at slower speeds in transparent substances. White light consists of a mixture of radiations with wave lengths between 4000 Å and 7000 Å. Wave lengths outside these limits are not visible to the human eye. Light of a wave length of 4000 Å appears violet and at 7000 Å, red. The other spectral colors occupy intermediate positions in the order: violet, blue, green, yellow, orange, red. (The human eye has a maximum sensitivity of approximately 5560 Å in the green.) Wave lengths longer than 7000 Å up to about 1 mm are called infrared rays. Still longer waves are known as radio waves. These may have wave lengths anywhere from 1 cm up to several miles. Light waves which are shorter than 4000 Å are known as ultraviolet light. Ultraviolet waves extend down to about 100 Å. Below this we get into the region of X-rays which extend below 1 Å (see Figure 2–2).

Light, and all electromagnetic radiation, also behaves as if it consisted of particles which move with an energy inversely proportional to their wave lengths. A particle of light is called a photon. Other particles, moving at velocities which approach the speed of light, also behave as if they were waves. A stream of electrons moving at high velocity can be regarded, for many purposes, as if it were a ray of light.

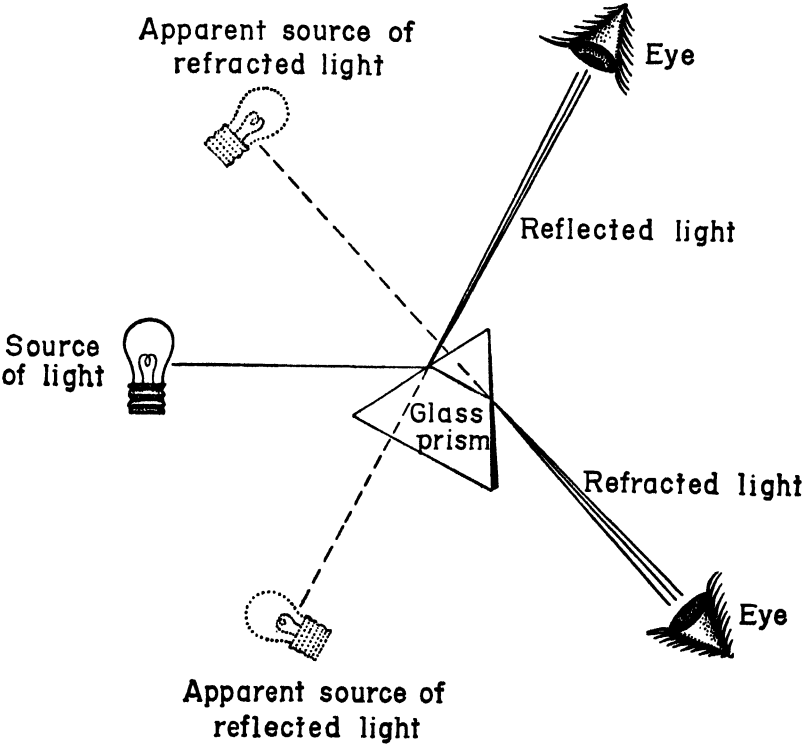
Apparent source of refracted light
Eye
Reflected light
Source of light
Glass prism
Refracted light
Eye
Apparent source of reflected light

FIG. 2-3. Reflected and refracted light.

We observe objects for one of two different reasons. We see a printed letter because it does not reflect as much light as does the page it is printed on; but we see a star because it sends light to our eyes. There are correspondingly two ways in which we can see an object in a microscope. We can illuminate the object from below and see those parts which absorb light as dark areas on a bright field, or we can illuminate it from the side and see those particles which reflect light into our eyes as bright spots on a dark field. The first method is used in most biological and medical microscopic work; the second, which is called the dark-field method, has been used especially by colloid chemists but is also useful in many other fields.

An object will absorb light if it contains pigments or is itself a pigment. Carbon black is an example of a pigment that absorbs nearly all the light which falls on it. Metals absorb or reflect almost all the light that falls on them, although very thin films of some metals are transparent. The vast majority of pure substances are colorless and are visible because they reflect or refract light. Any object having a refractive index which differs from the refractive index of the medium surrounding it will be visible. We can see a transparent glass prism for two reasons. One is that it reflects light at its surface; the other is that light which passes through the prism is refracted or bent so that objects appear to be displaced (see Figure 2-3).

A grain of sugar is transparent and we see it primarily because it reflects light into our eyes. A bowl of sugar is white because each crystal reflects light from a different angle and the net impression is that of whiteness. All white objects appear white because they reflect light from many different angles. Blue crystals of copper sulfate appear much whiter when the crystals are finely powdered because powdering increases the number of reflecting surfaces.

The fraction of the incident light which is reflected by a particle depends upon the angle of incidence and upon the difference between the refractive indices of the medium and the particle. Likewise, the extent of refraction depends on the difference in the refractive indices of the substances through which the light passes, and also on the angle of incidence. The angle of incidence will take all possible values when we deal with a powder, but we do have control over the index of refraction.

If we immerse a particle in a liquid which has exactly the same refractive index, the particle will neither reflect nor refract light and, if it is transparent, it will be invisible. You can demonstrate this effect with glass wool or cotton fibers. These materials have refractive indices which lie between the refractive index of benzene, 1.501, and that of bromobenzene, 1.560. By adding benzene in small increments to bromobenzene it is possible to obtain any desired refractive index within that range. If a glass fiber is immersed in bromobenzene and benzene is added slowly, a point will be reached where the fiber no longer reflects light and may be quite invisible. Substances whose refractive indices have an optical dispersion very different from that of the medium will appear colored when they are immersed in a solution whose refractive index is the same at one wave length but not at longer or shorter wave lengths. The first criterion for visibility of transparent particles is that they have a refractive index which differs from the refractive index of the medium.

A small particle will naturally reflect less light than a large particle. Raleigh has shown that the intensity of the light which is reflected from a very small particle falls off as the square of the volume of the particle. The number of particles in a suspension of a given concentration is inversely proportional to the volume of the particles. Therefore the total amount of scattered light will be proportional to the volume of an individual particle. Debye[1] has derived an equation relating the scattering of light by solutions of very small transparent particles to the osmotic pressure of the solution. The intensity of the scattered light for solutions of proteins and high polymers is very low and can be measured only by very careful techniques. Some idea of the size and shape of larger particles can be obtained from measurements of the scattering of light at various angles, but there are many technical and theoretical difficulties still to be overcome.

Light from a point source is not focused to an exact point by any optical system. The image of a point source is always a spot of light which is frequently surrounded by a set of rings or halos. This phenomenon is called diffraction and is a consequence of the wave nature of light. If two point sources of light are closer together than one quarter of the wave length of the light, the image of the two will not be distinguishable from the image of a single spot even with the best optical equipment. The size of the diffraction spot and rings is proportional to the wave length of the light and inversely proportional to the size of the half angle of the cone of light which is received by the first lens. This angle is the angular aperture ϕ (see Figure 2–4).

When ϕ is small, as in the case of narrow slits or small apertures, the diffraction spots are large and the resolution is poor. By resolution we mean the minimum separation of two point sources which can just be distinguished in the image. The resolution, r, is given by the following equation,

$$r = \lambda/2n \sin \phi \qquad (2\text{–}1)$$

where λ is the wave length, n is the refractive index of the medium, and ϕ is the angular aperture. The term $n \sin \phi$ is called the numerical aperture, N.A. The very best microscopes have an angular aperture close to 90°, and the object is immersed in an oil having a refractive index of 1.5. If we use yellow light of 6000 Å wave length,

$$r = 6000/2 \times 1.5 \times 1 = 2000 \text{ Å}.$$

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[1] Debye, P., *J. Applied Physics* **15**, 338 (1944); **17**, 392 (1946).

The ultimate resolution of a good light microscope is therefore about 2000 Å or 0.2μ. If we use violet light we can lower this to about 1300 Å, but it is much harder to see the image. Ultraviolet light can be used for photography but it requires special lenses and focusing is difficult and tedious.

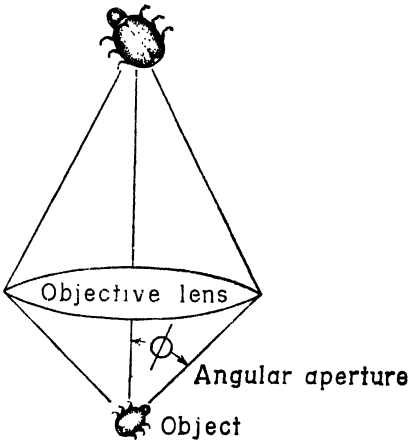

FIG. 2–4. The numerical aperture, ϕ, of a simple lens.

We see, therefore, why the limit of useful magnification in a microscope is 1000 times. At this magnification a pair of points 0.2μ apart appear to be 0.2 mm apart which is close to the limit of resolution of a normal eye. Any further magnification will only increase the size of the blurred image without increasing the definition.

Electron Microscopes.—An electron microscope is an instrument which uses beams of electrons instead of light rays to produce an image. Electrons are given off by hot metals and will be attracted by a positive electrode or anode. If the anode has a hole in it some electrons will pass through the hole as a beam of electrons, or a cathode ray. This beam of electrons has many of the properties of a beam of light. It can be bent or refracted by electrostatic or magnetic fields. A circular electrostatic or magnetic field behaves as a lens which will focus the beam of electrons and produce an image of the source of electrons.

An electron microscope has the same essential components as a light microscope. These are illustrated in Figure 2–1c. There is a source of high velocity electrons, and a condensing lens to focus the beam on the object. An objective lens makes an image of the object which is further magnified by the projection lens. The final image is formed on a fluorescent screen or on a photographic plate.

Electrons are scattered or absorbed by all matter including gases. It is, therefore, necessary to evacuate the entire electron path. The object and the image screen or plate must also be in the evacuated chamber. The necessity for operating in a vacuum imposes a severe limit upon the material which is suitable for examination. Only completely dry objects can be used because water or other solvents would evaporate in the vacuum. This means that living specimens cannot be observed (the beam of electrons would kill them even if they survived desiccation). Nor is it possible to examine colloidal solutions. We are limited to dry materials such as dust and smoke, dried particles from suspensions, and thin films.

The thickness of a specimen is also limited by the fact that all matter absorbs and scatters electrons. A film 5000 Å thick is about the upper limit for successful electron microscopy. Some specimens can be stuck to fine wire screen and observed without any other support but most specimens must be supported. The usual supporting medium is a film of collodion (see page 165), although Formvar, polyvinyl formal (see page 137), is said to be stronger. Either of these substances may be dissolved in a suitable solvent and spread to a thin film on a dish of water. The solvent evaporates and leaves a film of plastic material only a few hundred Å thick. This film is fished up on a fine wire screen which is mounted in the electron microscope. Drops of suspensions may be evaporated on these thin films and the suspended material will remain on the surface of the film.

Among recent developments in this field is the use of thin replica films which may be cast on the surface of a solid to be investigated. The top surface of such a film will be flat but the bottom surface of the film faithfully follows the contours of the surface on which it is cast. The replica film is thin enough to be examined in an electron microscope. The contrast of replica films, and of other materials supported on replica films, may be increased by evaporating a very thin layer of gold or other metal on the surface. If the atoms of evaporated metal come obliquely from one side, they will leave "shadows" behind projections on the surface where the metal atoms did not condense on the film. The length of these shadows is proportional to the height of the projection but may be as much as ten times longer, just as your shadow before sunset is longer than your body. The paper quoted in the footnote[2] is a valuable summary of the shadowing technique and contains many references to other work in this field.

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[2] Williams, R. C., and Wyckoff, R. W. G., *J. Applied Physics* **17**, 23 (1946).

The best resolution which can be obtained in an electron microscope appears at present to be about 15 or 20 Å. Electrons behave as waves, especially when they are moving rapidly. The wave length is inversely proportional to the velocity; therefore, such rapidly moving electrons behave as if they were waves of a short wave length. The effective wave length of an electron can be expressed as $\lambda = \sqrt{150/v}$ where λ is the wave length in Å and v is the accelerating voltage. Most modern electron microscopes use a voltage of 30,000 to 100,000 volts to accelerate the electrons and the corresponding values of λ are below 0.01 Å. We might expect that an electron microscope would have a resolution of the same order, or at least a resolution of 1 Å which would enable it to "see" individual atoms. Unfortunately, the aberrations of electron lenses are so much greater than the aberrations of lenses for use with light that only very small angular apertures can be used. The numerical aperture of most electron microscopes is about 0.001, whereas a good microscope has a numerical aperture close to unity for observations in air, and up to 1.5 for observations under oil. The small numerical aperture sets a theoretical lower limit on the resolution of about 10 Å. In actual practice it is difficult to obtain resolution better than 30–50 Å.

Further improvements may be expected in the resolution of the electron microscope but it is very doubtful whether we will ever see an atom as more than a blurred spot, if only because of the fact that even in solids the atoms are vibrating with extreme rapidity.

The useful range of the electron microscope, from 30 Å up to 2000 Å, corresponds almost exactly to the range of colloidal dimensions. It should be realized, however, that only a fraction of the colloidal systems which are dealt with in this book can be studied in the electron microscope, because it is not suitable for the examination of liquids. The electron microscope is one tool for the investigation of colloids but there are many other tools. No one tool is complete in itself and, indeed, reliance upon one method of investigation has led many an investigator astray. It is only when we compare the results of several different types of investigation on the same system that we are justified in assuming that we understand that system.

Figure 2–5 illustrates the effect of resolution on the useful magnification. Successive stages of magnification of a photographic film are shown. The third picture at 250 times shows the individual grains of the emulsion as small dots. The fourth picture is magnified 2500 times but the only effect has been to enlarge the size of the grains without showing any more detail. The last picture was taken with an electron microscope at 25,000 times. The increased resolu-

A

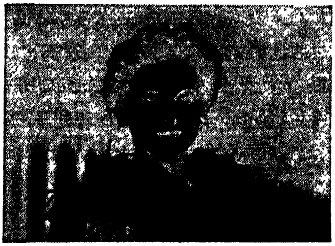

Fig. 2–5A. Here is a developed image.

B

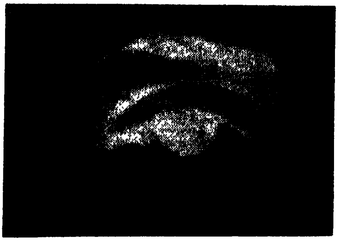

Fig. 2–5B. Magnified 25 diameters the silver grains are visible.

C

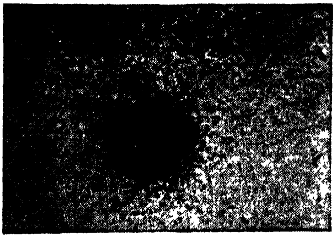

Fig. 2–5C. Magnified ten times more the separate grains can be seen.

D

Fig. 2–5D. When magnified 2,500 diameters the shape of individual grains can be seen.

E

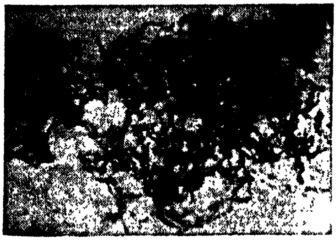

Fig. 2–5E. The electron microscope shows the developed grains to consist of filaments of metallic silver.

(Courtesy of Eastman Kodak Co.)

tion is immediately apparent and we see that each grain of the emulsion consists of twisted filaments. The previous picture gave no hint of this structure.

The advantages of the electron microscope lie not so much in the increased magnification of the original image as in the much greater resolution which is possible. Many electron microscopes work at lower magnifications than good light microscopes. The picture which is produced can, however, be magnified optically to the limit set by the resolution of the electron beam.

Ultramicroscopes.—The ultramicroscope is a microscope arranged so that light illuminates the object from the side instead of from below. No light from the source reaches the eye and particles which reflect light are seen as bright specks against a dark field. For this reason the ultramicroscope is frequently called a dark-field microscope. Most microscopes can be adapted to dark-field operation by adding a dark-field condenser. The original slit ultramicroscope, which was used by Zsigmondy, had an auxiliary microscope which concentrated a beam of light on the object field of the second microscope (see Figure 2–6). Particles smaller than the limit of resolution of the microscope will be visible if the illumination is sufficiently intense.[3]

Early workers with the ultramicroscope used sunlight reflected from a heliostat mirror into the condensing microscope. Arc lights are used more frequently, but most microscope lamps are not bright enough to show the smaller particles. High magnification is not essential in an ultramicroscope; indeed, the light which is scattered by colloidal particles can be seen most conveniently without any magnification at all. When a colloidal suspension, such as colloidal gold, is illuminated from the side by an intense beam of light, the path of the light is made visible by reflection from each particle. Faraday observed this phenomenon, and correctly ascribed it to reflection from particles. Tyndall's name is more commonly associated with the effect because he studied it and popularized it in his lectures and books.

The Tyndall cone is observed when light passes through a suspension of particles. Dust and smoke particles in the air, although they are not of colloidal dimensions, show a Tyndall cone. Many of the classical colloidal preparations, especially lyophobic suspensions of metals, salts and hydroxides, show the Tyndall cone. There is, however, a great class of colloids—those highly solvated in solution—which do not show the Tyndall effect because their refractive index is almost identical with the medium and they do not scatter light. Solutions of proteins and other high polymers come in this category.

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[3] Other models of dark-field microscopes are described in the general references referred to on page 41 and 42.

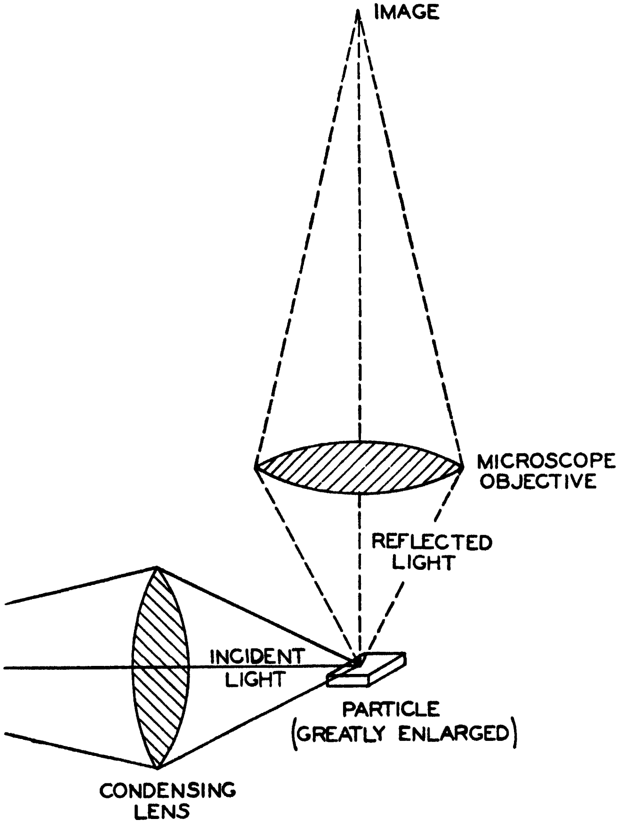

FIG. 2–6. Diagram of the path of the light rays in a Slit-Ultramicroscope.

The smallest particle which has been reported to be visible in the ultramicroscope is a colloidal gold particle 60 Å in diameter. The size of particles seen in the ultramicroscope cannot be determined from the size of the image. The average size of particles in a suspension can be calculated from the total number of particles in a given volume, which can be counted in an ultramicroscope, and the total amount of suspended material, which can be obtained by evaporating some of the suspension to dryness, or by other chemical methods.

X-Ray and Electron Diffraction.—X-rays are light waves which have wave lengths of the same order of magnitude as atomic radii. Unfortunately, X-rays cannot be refracted by any material because their wave lengths are of the same size as the atoms. An X-ray photon passes straight through most atoms in its path but eventually it may strike an atom "square on." The atom which is struck may reflect the X-ray or it may absorb the energy and re-emit X-rays or other radiation of greater wave length and less energy.

Since it is impossible to refract X-rays and since they cannot be bent in a magnetic or electric field, it does not seem possible to use X-rays to "see" atoms and molecules. X-rays are, however, scattered from atoms and a regular array of atoms, such as occurs in a crystal, will scatter X-rays in a regular pattern. The "reflection" of X-rays by the atoms is shown in Figure 2–7. "Reflection" takes place under the usual conditions of optical reflection and the added condition that

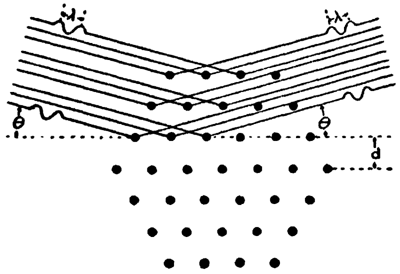

FIG. 2–7. "Reflection" of X-rays (of wave length λ) by a set of atomic planes (of spacing d) in a crystal. (From Huggins, *Frontiers in Chemistry* 4, Interscience (1945).)

$$\sin\theta = n\,\lambda/2d \qquad (2\text{–}2)$$

where n is an integer, 1,2,3, etc., and the other terms are defined in the figure. This last condition arises from the fact that X-rays are scattered by a series of points and reinforce each other only when equation 2–2 is satisfied.

When a crystal is placed in a beam of X-rays each possible plane which can be passed through a number of atoms in the crystal will produce a series of dots obeying equation 2–2. The resultant picture is a Laue diagram such as is illustrated in Figure 2–8. It is possible to calculate from such a diagram an arrangement of atoms which would produce the same X-ray picture and which is presumably the real structure of the substance. The calculation of the structure of crystals from X-ray data becomes more complicated the more atoms there are per molecule in the crystal. Huggins and his collaborators at the Eastman Kodak Company have prepared a series of photographic masks which permit a photographic integration of X-ray data to produce a representation of the unit cell of the crystal. The unit cell contains one or more molecules and the pictures frequently show the molecule with a resolution of a fraction of an Å. Figure 2–9a shows a reproduction of a hexamethyl benzene molecule obtained from its X-ray diagrams. For comparison, Figure 2–9b shows a photograph of a Hirshfelder atomic model of the same molecule and Figure 2–9c shows the conventional structural formula.

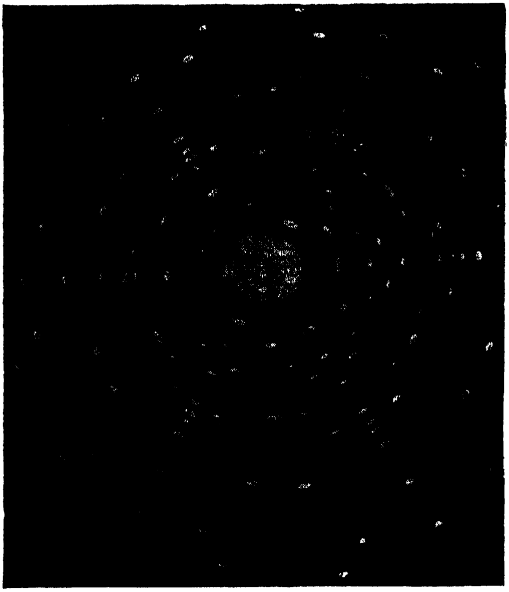

FIG. 2–8. Laue photograph of β Alumina. (From Huggins, *Frontiers in Chemistry* 4, Interscience (1945).)

Not all substances produce as sharp X-ray diagrams as the ones shown and it may be extremely difficult to decide upon a structure for more complicated substances on the basis of X-ray data alone.

When a powdered substance is irradiated by an X-ray beam, each crystal in the powder scatters the rays independently, and the picture produced consists of a series of rings or halos. Figure 2–10 shows three powder diagrams of different substances. Powder diagrams are like fingerprints and many substances can be identified by their powder diagrams. When two or more substances are present in a mixture the powder diagram will contain a set of rings corresponding to each substance present.

Most fibers consist of long molecules which are arranged in a crystalline structure with the long axis of the crystals parallel to the axis

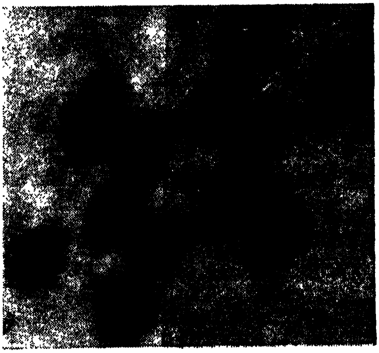

Fig. 2–9a. **Reproduction of the** electron distribution in hexamethyl benzene from its X-ray diagram. (From Eastman Kodak Co. An Advertisement in 1944–45.)

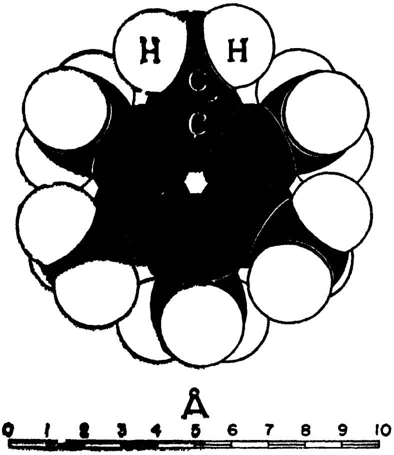

Fig. 2–9b. **Drawing** of a Hirshfelder model of hexamethyl benzene.

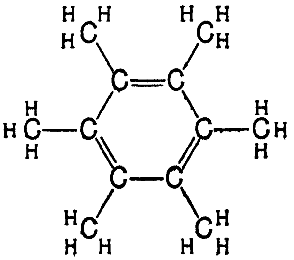

Fig. 2–9c. Structural formula of hexamethyl benzene.

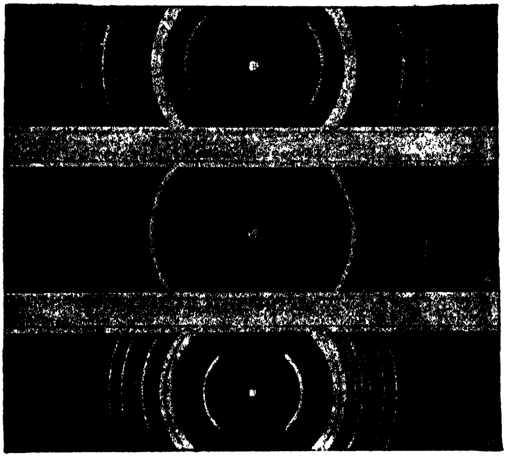

FIG. 2–10. X-ray powder diagrams. (1) Fe_2O_3, (2) Fe_3O_4, (3) $Ag_2C_2O_4$. (From Huggins, *Frontiers in Chemistry* 4, Interscience (1945).)

of the fiber. A collection of long crystals such as this gives a diffraction photograph which is similar to the Laue diagram of a single crystal (see Figure 2–11). Most fibers contain some unoriented material which produces diffuse halos in the diagram. The relative proportions of oriented crystals and unoriented matter can be estimated from the relative intensities of the spots and the diffuse halo.

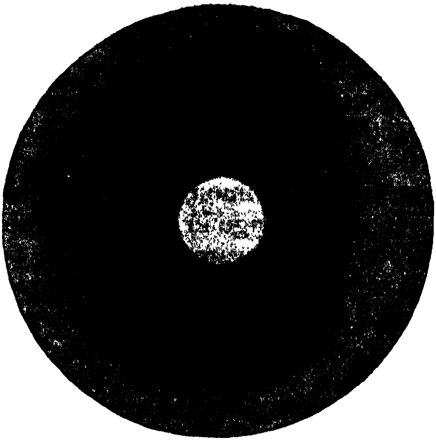

FIG. 2–11. X-ray fiber diagram of silk. (From K. H. Meyer, *High Polymers* 4, Interscience (1942).)

The sharpness of a Laue spot or of the ring of a powder diagram is inversely proportional to the size of the crystal which produced it. The broadening of the X-ray lines is inappreciable for crystals more than 500 atoms across, and reaches its limit in the diffuse halos of completely unoriented matter. Crystals less than 5 atoms across give such broad lines that the patterns are not recognizable. It is theoretically possible to deduce the size of crystals by this method, but there is no way of determining whether the particles consist of single crystals or of a number of imperfect crystals which have grown together.

Electrons are scattered by atoms in much the same way as X-rays, and electron diffraction photographs provide much the same sort of information as X-ray photographs. Electrons are, however, scattered to a much greater extent by matter, and do not penetrate very deeply. Electron diffraction patterns are thus most useful for studying the surface structure of solids since they do not penetrate more than a thousand Å in dense materials.

Ultrafiltration and Dialysis.—One very obvious way of determining the size of a particle is to find out how large a hole will just let it pass through. Standard screens are available for classifying particles larger than a few hundredths of a millimeter in diameter. The diameter of particles which will pass one screen and will be retained on the next smaller obviously lies between the mesh openings of the two screens. Long needle-like particles will have great difficulty passing through screens which are just large enough to pass them end on. It is not practical to use screens for dry particles smaller than 40μ. The study of particles in a size range between 1 cm and 1μ is ordinarily not included in the definition of colloid science, although the subjects have much in common. Dallavalla[4] presents a comprehensive treatment of the subject of powders and fine grains.

Although dry particles of colloidal dimensions cannot be graded to size by sieving, the same principles can be applied to particles in solution. Filtration is one common form of wet sieving. Ordinary filter paper has pores which range in diameter from 1 to 5μ (10,000–50,000 Å), and porous earthenware filters have pore sizes down to 1000 Å. Filtration is therefore one method which can be used to separate coarse granules from a suspension of particles of colloidal dimensions.

Filtration is not always a completely satisfactory method for separating particles because many substances clog up the pores of a filter and reduce their effective diameters. This is particularly true for flocculant precipitates which consist of a large number of small particles loosely bound together, such as a precipitate of ferric hydroxide.

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[4] Dallavalla, J. M., *Micromeritics—The Technology of Fine Particles*, Pitman, New York (1943).

Ultrafilters are membranes whose pore diameter is less than 1000 Å and the term is most frequently applied to filters with a pore size in the neighborhood of 20 Å. Such a filter will pass most noncolloidal molecules and will retain most colloidal substances. Most ultrafilters are made from collodion (cellulose nitrate) or from regenerated cellulose in the form of Cellophane or Visking (see Chapter 8). There are also mineral ultrafilters which have been prepared by filling the holes of porous earthenware with colloidal precipitates. All-metal filters, produced by electroplating a screen until the holes are almost filled up, have also been tried.

Membranes of Cellophane or collodion are clear and transparent because the holes are too small to scatter much light. These membranes also appear to hold water because the rate of flow through the membrane is so slow. The rate of flow of a liquid through a capillary, according to Poiseuille's law, is proportional to the fourth power of the radius of the tube. If the total filtration area is kept constant this means that a piece of filter paper with 10,000 Å pores will pass a given amount of water 1,000,000 times as fast as a piece of Cellophane with pores only 10 Å in diameter.

The pores of natural membranes are not all the same size; any membrane contains some pores larger and some smaller than the average size. If we use a membrane to separate particles according to size, the diameter of the largest pores is obviously of greatest interest and the presence of smaller pores is of little consequence. The pore size of a membrane can be estimated from the size of the particles which pass through it. This might be measured for a set of standard suspensions of known diameter, and these suspensions could then be used to calibrate new membranes.

The pore diameter can be estimated more conveniently from the pressure necessary to force air, or mercury, into a wet membrane. This method depends upon the fact that surface tension produces a greater pressure inside a drop or bubble than exists outside. Surface tension will be discussed in the next chapter; it is a tension which exists at the surface between any two fluids. The surface tension acts to reduce the area of the surface. The pressure produced inside a spherical drop or bubble is inversely proportional to the diameter of the sphere.

$$P = 4\gamma/d \tag{2-3}$$

where P is the excess pressure inside the sphere, γ is the surface tension and

d is the diameter. (Equation 2–3 is frequently written $P = 2\gamma/r$, where r is the radius.)

If numerical values are substituted in equation 2–3 we find that, when water wets the pores, the pressure necessary to force air or nitrogen through pores 1000 Å in diameter is 420 pounds per square inch (p.s.i.). The calculated pressure necessary to force air bubbles through holes 10 Å in diameter is 42,000 p.s.i. The method cannot, however, give reliable values at such high pressures, if only because of the solubility of the gas in water.

The surface tension of water is 72 dynes per cm at 20° C. With pores 1000 Å, or 10^{-5} cm, in diameter the pressure would be $4 \times 72/10^{-5}$ which equals 2.88×10^7 dynes per cm^2. This may be converted to atmospheres by the factor 9.86×10^{-7} or to pounds per square inch by the factor 1.45×10^{-5}.

Thin fragile membranes must be supported on fine wire screens if they are to withstand high pressures. It is frequently possible to make ultrafilters inside the pores of stronger, more porous, substances. Collodion films may be made in the meshes of cloth, or filter paper, or in the wall of a porous cup. It is not possible to prepare membranes in this way whose properties are as reproducible as the properties of flat membranes. Elford[5] has described a very elaborate procedure for preparing collodion membranes of reproducible pore size in the range 100 Å to 10,000 Å (1μ).

The pore size of collodion membranes may also be controlled in the range from 2 to 100 Å by soaking them in solutions of alcohol and water.[6] When a solution of collodion in alcohol and ethyl ether is dried the pores become so small that they will pass water, and ions such as K^+ and Cl^-, only with difficulty. When a dried membrane is soaked in a solution of alcohol and water, the pores open up, and they will remain open so long as the membrane is not allowed to dry out. The size of the pores increases with the concentration of alcohol in which the dried membrane has been soaked. Membranes which have been soaked in 80% alcohol will pass small molecules and unassociated dyes, such as methylene blue and safranine, but not particles with molecular weights greater than about 1000. Soaking in 95% alcohol produces membranes which are permeable to many colloidal dyes such as Congo Red.

A less reliable way of obtaining membranes with pores which are large enough to pass small molecules but not colloids is to plunge the membrane in water before it is completely dry. A 4% solution of collodion is poured into a test tube and poured out again. The tube is drained in an inverted position for 10 or 15 minutes (the time of drying controls the pore size) and then filled with water. The membrane comes loose from the walls of the tube and can be used for dialysis tests to distinguish between colloidal and crystalloidal dyes.

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[5] Elford, W. J., *Trans. Faraday Soc.* **33**, 1094 (1937).

[6] Brown, W., *Biochem. J.* **9**, 591 (1915).

The use of ultrafilters to determine pore size is subject to the same limitations as ordinary filtration. Many substances stick to the surface of the pores. This may clog them so that the membrane becomes impermeable to the substance being tested even though the pores are large enough to let through other particles of the same size. The theory of ultrafiltration is discussed by Ferry.[7]

The most frequently used membranes for ultrafiltration at the present time are collodion, and Cellophane or Visking. Many others have been tried. Parchment paper, which is produced by treating paper with sulfuric acid, was used in most early work. Animal bladders and skins, both of which are protein materials, have also been used. Many of the newer plastic materials have been tried but none of them have the desirable combination of properties which is found in collodion. Collodion is a 4% solution of cellulose nitrate in a mixture of 75% ethyl ether and 25% ethyl alcohol. Regenerated cellulose, as Cellophane or Visking, is the most convenient substance to use, although the pore size is a little small. Commercial Cellophane in water will not pass any colloidal substances and will even slow up the movement of small molecules such as sucrose.[8]

Sedimentation.—It is well known that light objects fall more slowly than heavy objects in air or under water. It is only in a vacuum that all bodies fall at the same rate. The force of gravity on any object is proportional to its weight, but the resistance to movement through a fluid is proportional to its area and to the viscosity of the fluid. Viscosity is a measure of the resistance of a liquid to flow.

Viscosity may be defined as the tangential force necessary to produce a difference in velocity of 1 cm per second between two parallel planes 1 cm apart which are immersed in the fluid. The unit of viscosity is the poise, or more usually, the centipoise which is equal to 0.01 poise. At 20° C. the viscosity of air is about 0.018 centipoise, water is 1 centipoise and pure glycerine is 1500 centipoises.

When a body is allowed to fall in a liquid, it quickly reaches a limiting velocity at which the resistance of the liquid exactly balances the pull of gravity. Stokes' law gives the terminal velocity of a falling sphere:

$$v = d^2 (\rho - \rho_0) g/18\eta \tag{2-4}$$

where v is the terminal velocity, d is the diameter of the sphere,

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[7] Ferry, J., *J. General Physiology* **20,** 95 (1936).

[8] McBain, J. W., and Stuewer, R. F., *J. Physical Chem.* **40,** 1157 (1936).

ρ and ρ_0 are the densities of the sphere and the liquid, g is the force of gravity, and η is the viscosity.

Stokes' law applies only to spheres which are much larger than the particles which make up the fluid. Very few particles are exactly spherical, but Stokes' law can still be used to give first approximation of the size of a particle from its rate of sedimentation. The rate of fall in water of a sphere 1000 Å in diameter having a density of 2 may be calculated as follows:

$$v = (10^{-5})^2 (2 - 1)\ 980/18 \times 0.01. \tag{2-5}$$

The velocity, v, equals 5.4×10^{-7} cm per second or 470μ per day. This rate of fall is so slow as to be almost unobservable and any slight convection currents will stir up the solution and prevent sedimentation. It is for this reason that colloidal particles do not settle out of solution.

Red blood cells are flattened and have a mean diameter of about 6μ or 60,000 Å. Their rate of sedimentation would be $(60)^2$ or 3600 times as great as the spheres considered above if their density were 2. The density is actually much closer to that of water, yet red cells do settle at a rate which can be measured in centimeters per hour. This rapid rate of sedimentation can be attributed entirely to the formation of piles of cells or rouleaux which settle rapidly.

When particles of different sizes are mixed to a uniform suspension in a liquid and then allowed to settle, the large particles will settle out more rapidly than the smaller particles. After a period of time the top layer of the solution will be free from particles; below this will be a layer containing small particles; and further down will be a region containing both large and small particles. The rate at which particles arrive at the bottom will be the sum of the rates of sedimentation of all the particles in the suspension. The distribution of equivalent diameters of the particles in a suspension may be obtained from a graph of the quantity settled out as a function of time by a method developed by Odén.[9]

The force of gravity is too feeble to produce rapid settling of colloidal systems. We can increase the effective accelerating force on a system by spinning it in a centrifuge. When an object is rotated around an axis at a distance r from the axis, the acceleration on the object will be $\omega^2 r$, where ω is the rate of rotation in radians per second.

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[9] Odén, S., *Alexander's Colloid Chemistry* **1**, 861 (1926). See also: Holmes, H. N., *Laboratory Manual of Colloid Chemistry*, p. 3 (1934); and Svedberg, T., *Colloid Chemistry*, pp. 176 ff. (1928).

The acceleration in a centrifugal field is frequently expressed in terms of the acceleration of gravity as G. One G equals 980 dyne cm per second and the value of G for a given centrifugal field is

$$G = \omega^2 r/980. \tag{2–6a}$$

The rotational speed in radians per second is $2\pi/60$ times the revolutions per minute, r.p.m. The formula for converting r.p.m. to G is, therefore,

$$G = (\text{r.p.m.} \times 2\pi/60)^2\, r/980$$

or

$$G = 1.12 \times 10^{-5} \times (\text{r.p.m.})^2 \times r. \tag{2–6b}$$

One of Svedberg's centrifuges operates at a speed of 70,000 r.p.m. and the center of the cell is 6.5 cm from the axis of rotation. The centrifugal acceleration is, therefore,

$$G = 1.12 \times 10^{-5} \times 6.5 \times (7 \times 10^4)^2 = 360{,}000 \text{ times gravity}$$

which is close to the maximum that can be sustained by a rotor which is designed to contain a sample under observation. A solid steel rotor 9 mm in diameter has been rotated at 1,200,000 r.p.m. corresponding to an acceleration of 7,000,000 G. This represents very nearly the theoretical upper limit for the best hardened steel. At this acceleration the stresses produced by the weight of the metal are sufficient to pull it apart. Lighter metals, such as the aluminum alloys, can be used to advantage even though their lighter weight is more than offset by their lower yield value. Duraluminum, for example, is much cheaper to machine than steel, and its lighter weight reduces the destructive power of the fragments if the rotor should burst.

Svedberg pioneered in the application of high centrifugal forces to the study of colloidal systems. He found that it was necessary to eliminate convection currents in any investigation of sedimenting suspensions. This can most conveniently be done by enclosing the suspension in a capillary or in a thin flat-walled cell. A centrifuge in which convection currents have been eliminated is called an ultracentrifuge. Low-speed ultracentrifuges are usually driven by an electric motor, with or without a gear train. High-speed ultracentrifuges for the study of sedimentation are of two types: the oil driven turbine, which is the product of Svedberg's laboratory; and the air-driven top.

Svedberg's oil-driven centrifuge receives its driving force from two streams of oil which are pumped at high pressure through small turbines located in the ends of the rotor shaft. Figure 2–12[10] shows the rotor of the high-speed ultracentrifuge for which the gravitational force was calculated earlier in this section. The auxiliary equipment

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[10] Boestad, G., Pedersen, K. O., and Svedberg, T., *Rev. Sci. Insts.* **9**, 346 (1938).

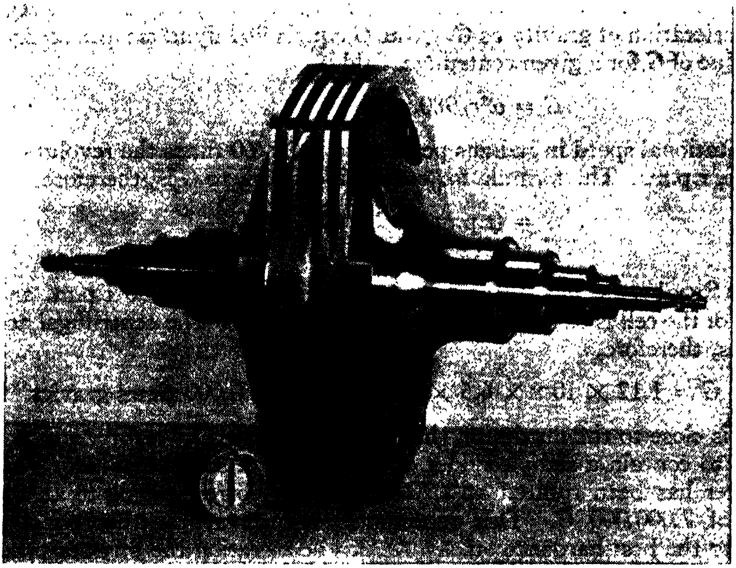

FIG. 2-12. The rotor of one of Svedberg's centrifuges, about one foot long. (From Boested, Pedersen and Svedberg, *Rev. Sci. Inst.* 9 (1938).)

to operate this centrifuge occupies most of two rooms and resembles the engine room of a small ship. It is obvious that, although centrifuges of this type have their place, they are not generally available in colloid laboratories.

Shortly after Svedberg began his studies on ultracentrifuges, Henriot and Hugenard described a new method of obtaining very high rotational speeds without the use of mechanical bearings. Their

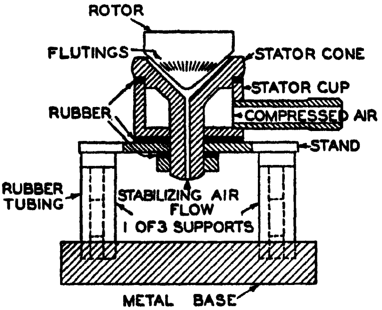

FIG. 2-13. Spinning top centrifuge, one to two inches in diameter. (From Pickles in *Alexander's Colloid Chemistry* 5, Reinhold (1944).)

centrifuge consists of a conical spinning top which is driven by jets of air which also support the top. Figure 2–13 shows one type of air-driven top. The spinning top is very easy to make and the complete equipment can be purchased for less than a hundred dollars. It does not, however, exist in thermal equilibrium because of the heat generated by friction of the air stream. This difficulty has led several workers to doubt the usefulness of this type of centrifuge because the thermal gradient will generate convection currents. McBain has solved this problem by a whole series of ingeniously designed inserts which reduce convection in some or all parts of the system.[11]

The small top is certainly adapted to chemical determinations of sedimentation and equilibrium, whereas larger rotors are more useful for optical observation and quantity preparations. The "simplest ultracentrifuge" consists of a rotor containing a capillary tube which is placed over a piece of sensitive photographic paper. The centrifuge is operated in the dark for a measured time; it is then illuminated with parallel light from above while the rotor is still running. The sedimenting material casts a shadow on the sensitized paper which is then developed and measured. The results obtained by this method are not quite so precise as those which could be obtained in larger centrifuges but the cost is very much less.

Bauer, Beams and Pickles[12] and others have combined the inexpensive air-driven top with the large rotors used by Svedberg. They hang the rotor by a steel wire from the air-driven top. The rotor is usually operated in a vacuum to reduce thermal gradients due to air friction, and the instrument provides a good compromise between the very expensive Svedberg model and the size limitations of the simple top. Figure 2–14 shows a diagram of a high-speed ultracentrifuge with a rotor supported in a vacuum.

The rate of sedimentation in a centrifuge is given by an equation similar to equation 2–3 with the appropriate value of G inserted. Since G varies with r, which is the distance from the center of the rotor, the velocity of sedimentation will also vary. This velocity divided by the accelerating force in dynes, $\frac{dr}{dt}\cdot\frac{1}{\omega^2 r}$, is the sedimentation constant and is denoted by s. The sedimentation constant is usually corrected to 20° C. for a fluid having a viscosity equal to that of pure water. When so corrected the sedimentation constant is written s_{20}. Since the units of the sedimentation constant are of the order of 10^{-13} c.g.s. units (cm $\times$ sec^{-1} $\times$ dyne^{-1} $\times$ gm $=$ sec), a new

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[11] McBain, J. W., *Chem. Rev.* **24**, 289 (1939).

[12] Pickles, E. G., *Rev. Sci. Inst.* **9**, 358 (1938); **13**, 101 and 426 (1942).

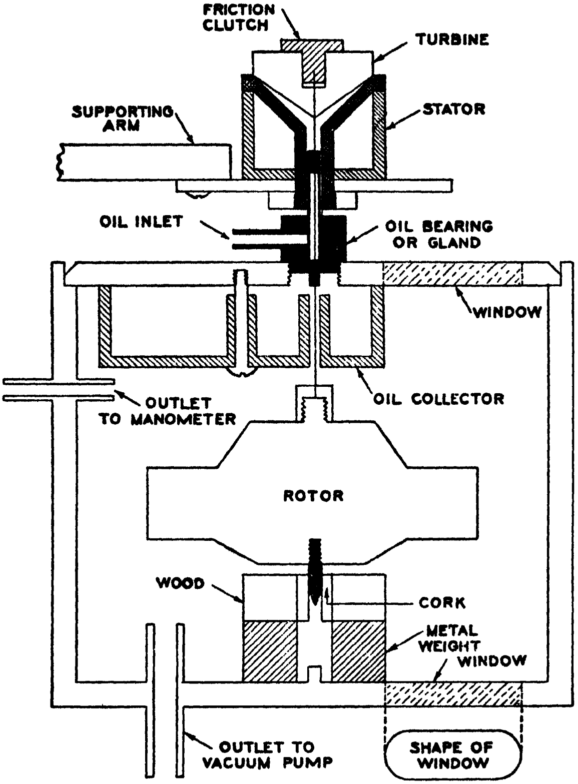

FIG. 2–14. Drawing of the first suspended rotor high speed centrifuge of the vacuum type. (From Pickles in *Alexander's Colloid Chemistry* 5, Reinhold (1944).)

unit, the Svedberg S, is defined as equal to 10^{-13} seconds. The size of spherical particles can be obtained from the sedimentation constant by making use of Stokes' law in the following form:

$$d^2 = 18\eta s/(\rho - \rho_0). \tag{2-7}$$

The molecular weight of a particle can be obtained from the sedimentation constant and the diffusion constant, D, on the assumption that the particle meets the same resistance to diffusion and sedimentation. Svedberg's formula for the molecular weight, M, of a particle is:

$$M = RT\,s\rho/D(\rho - \rho_0) \tag{2-8}$$

where R is the gas constant and T is the absolute temperature. The derivation of this law is given in Svedberg's *Colloid Chemistry*, in Svedberg and Pedersen's *The Ultracentrifuge*, and in Pickles' article (see the references at the end of this chapter).

PHYSICOCHEMICAL METHODS

There are a number of physicochemical methods for determining the size of a colloidal particle. All these methods depend upon the fact that all suspended particles, regardless of size, have the same translational kinetic energy. The first indication of this fact came from the observation by Robert Brown in 1826 that small pollen grains suspended in water were continuously in motion. Further investigation showed that all small particles exhibit this random dancing motion, and also that the motion was not due to external causes. The motion was later shown to be caused by the random impacts of molecules in the solution on the particle. Albert Einstein in 1906 deduced the laws of Brownian motion from the assumption that all particles in a solution or a suspension have the same average kinetic energy.

The translational kinetic energy per mol of any gas is $3/2\ RT$, where R is the gas constant and T is the absolute temperature. The translational energy of molecules in a liquid is the same as in a gas; the difference in energy between a liquid and its vapor lies in the elastic forces between the molecules. The average translational kinetic energy of a molecule is therefore $3/2\ RT/N$, where N is Avogadro's number, or the number of molecules in a mol. The value of N is 6.023×10^{23}. It is convenient to substitute R/N by a new constant, the molecular gas constant or the Boltzman constant, k, which equals 1.380×10^{-16} ergs per degree. The average translational kinetic energy of any particle in a liquid is therefore $3/2\ kT$.

Since translational kinetic energy is $1/2\ mv^2$, where v is the velocity and m is the mass of a particle, we should be able to determine m from the average velocity of Brownian movement. A direct measure of the rate of movement is, however, impossible since a particle will change direction about 10^{13} times a second. We can, however, measure the mean displacement from an initial position and we find that this displacement is proportional, not to the time, but to the square root of the time. Calculations based on probability theory show that this is what we should expect if a particle makes a very large number of random movements during the interval between observations. The square of the amplitude of movement, a, is given by the following equation, which was developed by Einstein:

$$a^2/t = 2\ kT/3\pi\eta d \tag{2-9}$$

where t is the time between observations. When a series of measurements are made, as is always necessary when dealing with statistical fluctuations, one must use the average of the values of a^2/t for each observation. Equation 2-9 is developed for spheres according to Stokes' law and is subject to the limitations of that law. The molecular weight can be obtained from the diameter of the particles and their density since the molecular weight is the weight of 6.023×10^{23} particles.

The term "molecular weight" has been used here in a sense which is open to some controversy. Objections have been raised against the use of the term molecule for a large particle. The usage is justified, in the opinion of the author, because large particles do, in fact, obey the same laws as small molecules. In this work we shall use two definitions of a molecule. The first is essentially that given above. The "kinetic molecular weight" is the total weight of the suspended material in atomic weight units, divided by the total number of independent kinetic units in the suspension. For rigid particles the kinetic molecular weight will be N times the average particle weight. The second definition is used in Chapter 6 and following chapters in the discussion of high polymers. A molecule is there defined as an assembly of atoms joined by covalent bonds. For many high polymer systems at extreme dilution the two definitions are identical.

The random Brownian motion of all particles in solution is responsible for the phenomena dialysis and diffusion. If a solution is placed inside a membrane which has pores large enough to permit the solute molecules to pass through, they will dialyze out into the surrounding solution. If we use a membrane which permits small molecules to pass but not large ones, we can separate the two without applying any filtering force. The random Brownian movement will move the smaller particles through the membrane. This method of purification of colloids is called dialysis and is one of the most powerful methods of preparing pure colloids.

An electrical current can be passed through a pair of membranes containing a colloid, and it will accelerate the removal of electrolyte impurities. This method is called electrodialysis. It is efficient only in systems which contain low concentrations of electrolytes. Since the only part of the potential drop which is effective is across the membrane wall, the rest of the cell should be as thin as possible.

When a solution is placed in direct contact with pure solvent, the molecules in solution will move into the pure solvent, and at first there will be none to move back. As more particles move out into the solvent some will also move back. The net rate of movement across a thin layer will be proportional to the difference in concentration on the two sides of that layer and inversely proportional to the thickness. This can be expressed as

$$\mathcal{Q} = D\,(c - c_0)/(x - x_0) \tag{2–10}$$

where $\mathcal{Q}$ is the rate of movement, $c - c_0$ is the difference in concentration, and $x - x_0$ is the thickness of the layer. In differential form, $\mathcal{Q} = D\,dc/dx$. D is the diffusion coefficient.

There are a number of methods suitable for studying diffusion. The classical method is to place a layer of solution under a layer of solvent and measure the concentration of different layers after one or more days. Diffusion is slow—of the order of 1 cm^2 per day for the faster moving electrolytes—and it is very difficult to eliminate convection currents in cells large enough to hold enough material for chemical analysis. Optical methods of analysis are available for pure substances but they are relatively expensive.

Diffusion can also be carried out in porous glass filter disks which immobilize the liquid and prevent convection. This method, which was first used by Northrup and Anson[13] and later developed by McBain and his students[14] and by others is summarized in an article by Gordon.[15] The same issue of the journal contains several other papers on the subject of diffusion.

Diffusion measurements are a method for measuring the average Brownian movements of kinetic molecules in solution and are thus one method for obtaining molecular weights. Einstein showed that the diffusion coefficient is equal to $1/2\ a^2/t$ for any kinetic molecule. This is true because a molecule may move with equal probability in the direction of the lower concentration or in the opposite direction, and therefore only one half of the random displacements produce diffusion. It follows that the diffusion coefficient of a sphere, in a very dilute solution, is

$$D = kT/3\pi\eta d. \tag{2-11}$$

The diffusion coefficient can thus be used to obtain an estimate of the effective diameter of a particle and from it the molecular weight. This method is not to be recommended as being very precise. It is difficult to obtain diffusion coefficients with an accuracy of 1% and, since the molecular weight is a function of d^3, the error in the molecular weight will be three times the relative error of the diffusion measurement. Diffusion measurements are especially useful because they can be used on mixtures of any complexity so long as there exists a specific analytical method for measuring the concentration of the diffusing molecule. The first estimate of the size of some plant hormones and of some viruses has been obtained from diffusion measurements.

In our study of sedimentation we neglected for the moment the possibility of a particle falling upward. Conversely, in our study of diffusion we did not consider the possibility that a particle would fall downward, the displacements caused by Brownian movement were supposed to be entirely random in direction. If we look at the numerical values we see why diffusion and sedimentation do not interfere for most systems.

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[13] Northrup, J., and Anson, M. L., *J. General Physiology* **12,** 543 (1929).

[14] McBain, J. W., and Dawson, C. R., *J. Am. Chem. Soc.* **56,** 52 (1934).

[15] Gordon, A. R., *Ann. New York Academy of Sciences* **46** (5), 285 (1945).

On page 30 we found that a particle with a diameter of 1000 Å would sediment at a rate of 5.4×10^{-7} cm per sec if its density were 2. A particle 100 times bigger would fall at a rate of 5.4×10^{-3} cm per sec or nearly 19 cm per hour. This is a readily observable rate.

The magnitude of the Brownian movement may be calculated according to equation 2–9. The mean square displacement of a sphere is

$$a^2/t = 2\,kT/3\pi\eta d. \tag{2–9a}$$

Substituting the values for the constants at 20°C. in water, we find that

$$a^2/t = 2 \times 1.38 \times 10^{-16} \times 293/3\pi \times 0.01d \tag{2–9b}$$

or

$$a^2/t = 8.6 \times 10^{-13}/d \quad \text{or} \quad a = 9.3 \times 10^{-7}\sqrt{t/d}. \tag{2–9c}$$

If the diameter is 1000 Å or 10^{-5} cm, the mean displacement produced by Brownian movement will be nearly 3×10^{-4} cm in 1 second or 3×10^{-3} cm in 100 seconds. This is a displacement which is easily visible in a microscope. Smaller particles will move proportionately faster and a molecule 10 Å (10^{-7} cm) in diameter will move 3×10^{-3} cm, or 30,000 times its own diameter, in 1 second. It is obvious that we can never hope to see small molecules in motion and that the electron microscope would be useless for observation on solutions even if a cell were made which was thin enough to permit observations on a solution.

From these numerical examples, we see that the Brownian displacement in 1 second is of the same order of magnitude as the rate of sedimentation for particles between 1000 Å and 10,000 Å (0.1μ and 1μ) in diameter. For larger particles the Brownian movement is negligible and for smaller particles the rate of sedimentation is negligible.

The rate of sedimentation of a particle depends upon the resistance of that particle to movement through the medium. Likewise, the diffusion coefficient also depends upon the same resistance to movement. Both the sedimentation and the diffusion equations, which were given for a sphere according to Stokes' law, can be stated in terms of a frictional coefficient, f. The diffusion coefficient, D, is inversely proportional to the frictional coefficient, as follows:

$$D = RT/Nf. \tag{2–12}$$

The velocity of sedimentation is also inversely proportional to the frictional coefficient and directly proportional to the molecular weight and the buoyancy factor.

$$V = M(\rho - \rho_0)g/\rho f \tag{2–13}$$

or the sedimentation constant,

$$s = M(\rho - \rho_0)/\rho f. \tag{2–14}$$

The molecular weight enters equations 2–13 and 2–14 because of the way in which f was defined in equation 2–12. It is customary to rewrite the factor $(\rho - \rho_0)/\rho$ as $(1 - \bar{V}\rho)$ where $\bar{V}$ is the partial specific volume of the solute. Equations 2–13 and 2–14 will now read:

$$V = M(1 - \bar{V}\rho_0)g/f \quad \text{and} \quad s = M(1 - \bar{V}\rho_0)/f.$$

We may combine equation 2–12 with 2–14 to obtain Svedberg's equation for the molecular weight,

$$M = RTs/D(1 - \bar{V}\rho_0). \tag{2–15}$$

The ultracentrifuge may also be used to measure M directly from the sedimentation equilibrium. The centrifuge is run until the number of molecules which are diffusing upward through any layer is equal to the number which are sedimenting down. It is possible to derive the law which governs this equilibrium in several different ways. It applies equally well to the pressure of gases in the atmosphere as a function of their height and to the distribution of a suspension of particles 10,000 Å in diameter, as was first demonstrated by Perrin.

In a gravitational field the ratio of the concentrations, c and c_0, at any two heights, h and h_0, is given by

$$ln\,(c/c_0) = Mg(1 - \bar{V}\rho_0)(h - h_0)/RT \tag{2–16}$$

and, in a centrifugal field,

$$ln\,(c/c_0) = M\omega^2(1 - \bar{V}\rho_0)(r^2 - r_0^2)/2RT. \tag{2–17}$$

The derivation of these equations for sedimentation equilibrium does not depend upon any assumptions regarding the rate of movement of particles and the equation is therefore independent of the shape of the particles. The partial specific volume, $\bar{V}$, of the substance can be obtained from the density of the solution at various concentrations. Molecular weights which are based on sedimentation equilibrium are direct measurements of the kinetic molecular weight and are entirely free of all assumptions regarding the shape of the particles. Molecular weights which are based on sedimentation constants are apt to be less reliable, especially if the particles are not spherical.

Osmotic Pressure and Related Measurements.—All independent particles in solution behave as molecules regardless of their size, and we ought to be able to calculate the molecular weight of a colloid in solution in the same way that we calculate the molecular weight of urea or other simple molecules. The osmotic pressure, the lowering of the freezing point, and the elevation of the boiling point are all properties which are, as a first approximation, directly related to the number of dissolved particles.

The most satisfactory explanation of these relations may be found in the study of thermodynamics, which gives the correct answers but does not furnish a physical picture of the mechanism. An approximate derivation can be carried out as follows:

We fix our attention on a given number of molecules of solute and solvent, say N molecules so that we have one mol of solution. (A dilute solution in water containing N molecules would have a volume of about 18 ml). Each molecule in this collection has the same mean kinetic energy. The total kinetic energy of the system will consist of the sum of the energy of the solvent molecules and the energy of the solute molecules. N molecules of pure solvent will, therefore, have more energy than the solvent molecules in N molecules of solution.

We may assume that the rate of evaporation from a liquid surface is proportional to the total kinetic energy of the solvent molecules, also that the rate of condensation depends only upon the partial pressure of the solvent molecules over the liquid. The kinetic energy of the solvent particles may be represented as an internal pressure in the liquid. Although it is impossible to measure the internal pressure directly it can be estimated for pure liquids from the energy of evaporation.[16]

The foregoing reasoning leads to the conclusion that the vapor pressure of solvent over a solution is lower than over the pure solvent. Since the boiling point is defined as the temperature at which the vapor pressure equals one atmosphere the boiling point of a solution will be greater than that of a pure solvent. It is likewise possible to show that the freezing point will be lowered if the frozen solvent separates out as a pure crystal.

When a solution is placed inside a sack which has pores large enough to permit the solvent molecules but not the solute molecules to pass, and this sack is immersed in pure solvent the solvent will diffuse into the sack. Diffusion will continue until the solvent molecules inside and outside have the same kinetic energy. We can increase the energy of all the molecules in the sack by applying pressure. The pressure which prevents any net diffusion of solvent into or out of the sack is the osmotic pressure. The diffusion of solvent into a solution is called osmosis.

The osmotic pressure may be calculated as follows. The extra energy which must be supplied to the solvent molecules is just the translational kinetic energy of the solute molecules. Since the translational kinetic energy is the same in a gas as in a liquid the energy required is the energy of the same number of molecules of a perfect gas in the same volume. Therefore, we must apply a pressure equal to the pressure which the solute molecules would exert if they existed as a perfect gas in the same volume.

$$P = nRT/V \tag{2-18}$$

or

$$P = cRT \tag{2-19}$$

where P is the osmotic pressure, n is the number of mols of gas and V is the volume. The concentration, c, in mols per liter equals n/V.

[16] Glasstone, S., *A Textbook of Physical Chemistry*, 2nd Ed., p. 479 (1946).

The osmotic pressure is the only one of the physicochemical properties of a solution which can be measured for colloidal systems. The changes in freezing and boiling points are far too minute to be detected. Even osmotic pressures are very low. Egg albumin molecules are small colloidal particles with a molecular weight of 40,000 and a diameter of 40 Å (see Chapter 9). A 1% solution would contain 10 gm per liter or 10/40,000 mols per liter. The concentration is therefore 2.5×10^{-4} mols and the osmotic pressure at 0° C. would be $22.4 \times 2.5 \times 10^{-4}$ or 5.6×10^{-3} atmospheres or 4.25 mm of mercury. This is an osmotic pressure which can easily be measured. However, in order to obtain accurate results it is necessary to make measurements at lower concentrations and extrapolate to zero concentration. A molecule with twice the diameter would produce only 0.55 mm of mercury pressure in a 1% solution and it is difficult to measure such low pressures with the desired accuracy. Osmotic pressures are useful, therefore, only for substances with molecular weights less than a few hundred thousand. The method is most useful for the measurement of the mean molecular weight of high polymers.

There are a few other specific methods for determining particle size. The viscosity of a solution of a high polymer is proportional to the length of the molecular chain as a first approximation. This is "Staudinger's law" which is dealt with more completely on page 129. Doty and Mark review the various methods which are available for determining the size and shape of large molecules in solution.[17]

General References

For recent articles on new methods refer to the files of the following periodicals:

Industrial and Engineering Chemistry
Industrial and Engineering Chemistry, Analytical Edition (*Analytical Chemistry*)
Journal of Applied Physics
Journal of the Optical Society of America
Journal of Scientific Instruments
Nature
Review of Scientific Instruments
Science

References to specific methods are given in the following lists. Reference should also be made to one of several good textbooks of colloid chemistry, such as:

E. S. Hauser, *Colloidal Phenomena*, McGraw-Hill, New York (1939). This book has an appendix on methods.
H. N. Holmes, *Laboratory Manual of Colloid Chemistry*, New York (1934).

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CHAPTER 3

LIQUID SURFACES

The Field of Force Around an Atom.—All colloidal systems are characterized by a large ratio of surface to volume. Now a molecule which is located on a surface does not have the same molecular environment as a molecule which is located in the interior of a particle. This difference in environment produces a difference in properties, and most of the characteristic properties of colloids can be attributed to their large surface area, and to the correspondingly large number of the molecules which are located in the surface. A small crystal of sodium chloride 0.28 mm across has 10^6 atoms in each direction since the distance between sodium and chloride atoms is 2.8 Å (2.8×10^{-8} cm). The crystal contains 10^{18} atoms of which 6×10^{12} are on the surface. This means that only 6 out of every million atoms are in the surface. In contrast cellulose is so porous that from one quarter to one half of the reactive hydroxy groups are available at the surface of the pores (see page 159).

Before we can understand the properties of molecules in the surface of a particle it is advisable to examine the forces which molecules exert upon one another. Molecules in a liquid have the same translational kinetic energy as molecules of a gas. This fact is demonstrated by the phenomenon of Brownian movement and has been discussed in Chapter 2. The kinetic energy of a molecule is $1/2\ mv^2$, where m is the mass of the molecule and v is its velocity. A molecule in a gas spends most of the time moving in free space and the time spent inside the field of force of another atom is a relatively minor fraction of the whole. In liquids the molecules are packed so close together that they are continuously in the field of force of other molecules. It is only when a molecule is equidistant between two other molecules that its energy is all in the kinetic form. At other times some of the energy is kinetic and the rest is the potential energy of deformation of the molecules which are in contact.

Since the molecules of a liquid move with the same velocities as the molecules of a gas (of the same molecular weight), there must be some very strong attractive force between the molecules of a liquid which holds them together. These forces are of the same type and magnitude as the forces which hold together the molecules of a crystal.

The strength of solid materials is a result of the forces which exist between molecules. The strength of a block of ice is the result of attractive forces between the water molecules which make up the ice. The same attractive forces act between the molecules of liquid water, and water which has been freed of air bubbles can support tensions as great as 2000 p.s.i.[1]

The bonds between the molecules of perfect crystal are broken only when a molecule sublimes or dissolves from the surface. This is in contrast to the state of affairs in a liquid where the bonds between molecules are being continuously broken and new bonds are forming in their place. In a liquid the molecules are vibrating with a frequency of about 10^{13} times a second, and once in about every 10,000 vibrations (or 10^9 times a second) a molecule will move to a new position.[2] We see that, although the molecules in liquids are free to move, they nevertheless spend most of their time bonded nearly as tightly to their neighbors as are the molecules of a crystal. On the other hand, the molecules of a liquid can move about and a liquid can easily change its shape.

The attractive forces which operate between molecules are frequently called van der Waals' forces because these forces are also responsible for the deviations of a gas from the perfect gas laws, and van der Waals developed one of the first equations to describe these deviations.

The van der Waals equation for a gas is:

$$(P + a/v^2)\,(V - b) = RT. \tag{3-1}$$

The term a/v^2 represents the attractive forces between molecules, which vary inversely as the square of the volume, and the term b is proportional to the volume occupied by the molecules.

The van der Waals attractive forces between atoms are extremely short-range forces. Atoms which are not bonded together by chemical bonds, as for example two chlorine atoms which are attached to two different molecules, will attract each other with a force, J, which is proportional to the inverse seventh power of the distance between the atomic centers, x.

$$J = Cx^{-7}. \tag{3-2}$$

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[1] Dean, R. B., *J. Applied Physics* **15**, 446 (1944).

[2] Eyring, H., and Powell, R. E., in *Alexander's Colloid Chemistry* **5**, 236 (1944).

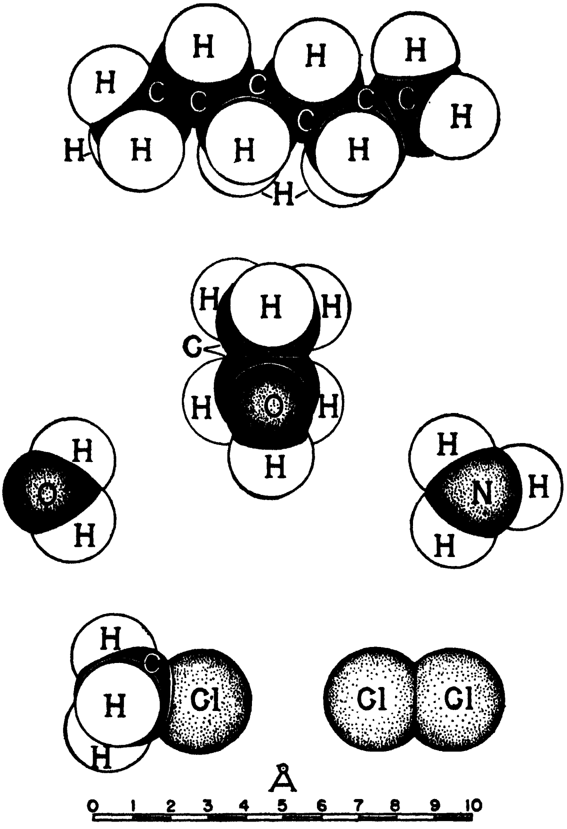

FIG. 3–1. Atomic models of hexane, ethyl alcohol, water, ammonia, methyl chloride, and chlorine.

C is a constant for any given pair of atoms. A force which falls off as the inverse seventh power gets rapidly weaker as the distance is increased. The centers of two chlorine atoms in two Cl_2 molecules can approach to within about 3 Å of each other. If the distance is increased to 4 Å the attractive forces between the atoms will be reduced to $(3/4)^7$ or approximately 13% of its value at 3 Å. At 6 Å the force will be only 0.78% of its value at 3 Å. This means that the attractive force between a pair of molecules is almost entirely the sum of the attractive forces between the atoms which are "in contact," and that the contribution of more distant atoms is negligible.

In addition to attractive forces between atoms there must also be repulsive forces. It is these repulsive forces which make solids and liquids so nearly incompressible. When atomic centers get closer than the atomic radius, a repulsive force, which varies approximately as the inverse thirteenth power of the radius, acts to hold them apart. For most practical purposes atoms behave like hard objects of constant volume. This atomic volume is represented by the *b* term of van der Waals equation. Figure 3–1 shows diagrams of a number of simple molecules. These diagrams, and others like them in this book, were drawn from photographs of molecular models which were developed by Dr. Hirshfelder to represent, as closely as possible, the external shape of a molecule.[3] You will notice how these models demonstrate that two atoms are much closer together when they are chemically united than when they are only in contact.

There are several kinds of attractive forces between atoms. The forces which vary as the inverse seventh power of the separation are by far the most important because they are effective between all kinds of atoms. Other forces which are important are the electrostatic attractive forces between ions, which vary as the inverse square of the distance between centers, and the attractive force between an ion and a dipole. Molecules which contain strongly electronegative ions such as F, Cl, O, and N will have an unsymmetrical distribution of electrons which is called a dipole. Water has a very strong dipole moment and therefore the oxygen atom of H_2O will be attracted toward positive ions, whereas the two hydrogen atoms will be attracted toward negative ions.

It is difficult, if not impossible, to give a physical picture of the attractive and repulsive forces between atoms. The forces are undoubtedly the result of the distribution of the electrical charges inside the atoms. The repulsive force arises from the fact that two charges of the same sign repel each other. When two atoms approach closer than their "collision radius," the electron orbits interpenetrate and the atoms are repelled from each other.

The attractive forces are, to a large degree, a result of the attraction which exists between opposite charges. Sodium ions and chloride ions are attracted together by these electrostatic forces in a crystal of common salt. Most molecules, however, are electrically neutral, and we cannot attribute their cohesion to simple ionic forces. If a molecule contains an electronegative atom (such as oxygen, nitrogen, or chlorine, or related atoms), this atom will attract more than its share of electrons. This will leave the other end of the molecule with less than its share of electrons. The entire molecule will behave as a dipole, which can be represented as a pair of charges separated by a short distance. For example, the electronic structure of methyl chloride may be represented as follows:

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[3] Supplied by the Fisher Scientific Co.

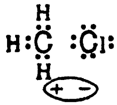

FIG. 3–2.

The resultant dipole is represented below the structural formula. The dipole of methyl chloride has a length of about 0.4 Å or 2 Debye units.[4] That is, it can be represented by two charges 0.4 Å apart.

Two dipoles will attract each other according to the same laws that govern the attractive forces between a pair of magnets. The ⊕ end of one dipole will attract the ⊖ end of another dipole and will repel other ⊕ poles. The average attractive force between rotating dipoles will vary as the inverse seventh power of the distance between centers. The attractive forces between permanent dipoles is responsible for the fact that polar liquids have higher boiling points than non-polar liquids of the same molecular weight. However, even molecules of non-polar liquids have a large attractive force and these forces cannot be due to the interaction of permanent dipoles. F. London suggested in 1930 that the attractive forces between atoms might be the result of temporary dipoles which are set up because the electrons are in motion and are not always symmetrically arranged around an atom. If there happens to be an excess of electrons on one side of an atom that side will become the negative end of a dipole. This dipole will induce dipoles in adjacent atoms and the net result will be an attractive force between the atoms. This is called the dispersion effect because the unsymmetrical distribution of electrons is also responsible for the phenomenon of optical dispersion.

The mathematical derivations of these forces, even for simple atoms, are very complicated. The results show that the dispersion effect is greater than the effect of permanent dipoles for all molecules except the most polar. Even in anhydrous hydrogen chloride the attractive forces are predominantly dispersion forces. Permanent dipoles are responsible for about half the attractive force between ammonia molecules and 80% of the attractive force between water molecules.

The dipole interaction between electronegative atoms which bear a hydrogen atom (such as —OH and —NH_2) and other electronegative atoms is so great that it has been dignified by the name of a "hydrogen bond." The hydrogen bond is very much weaker than other chemical bonds and it is perhaps better to consider it as the strongest type of molecular attraction rather than the weakest chemical bond.[5] The hydrogen bond is discussed in greater detail in Chapter 6.

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[4] Glasstone, S., *A Textbook of Physical Chemistry*, p. 551 (1946).

Molecules in a crystal usually attract molecules of the same kind more strongly than they attract dissimilar molecules. If this were not true it would not be possible to purify substances by recrystallization. The reason for this apparently specific attractive force is that a collection of units which are all the same size and shape will fit more closely together than a mixture of units of many different sizes. The attractive forces between molecules depend upon the number of points of contact between the atoms; the more closely the molecules fit together, the greater will be the attractive force. When two different molecules have the same size and shape they will crystallize together as mixed crystals, and no amount of fractional crystallization can separate them. A bromine atom and a methyl group have almost exactly the same size. Bromobenzene and methyl benzene (toluene) therefore crystallize together as mixed crystals.

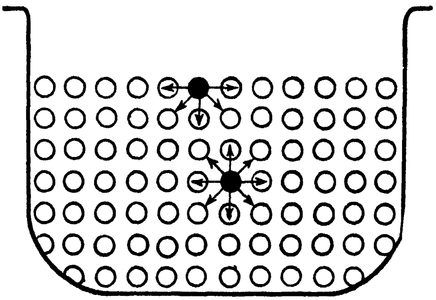

FIG. 3–3. Attractive forces on molecules in the body of a liquid and in the surface.

The Forces at the Surface of a Liquid.—A molecule inside a liquid is attracted with equal force in all directions. A molecule at the surface of a liquid is pulled down and sideways but there is no force pulling it up. This is indicated diagrammatically in Figure 3–3. As a result of these unbalanced forces the molecules in the surface will be pulled down into the liquid and the surface of the liquid will tend to grow smaller. An isolated body of liquid has a minimum area when it is a sphere, and we find that small drops of liquids are spherical. Large drops are distorted by other forces besides surface tension, and the shape of a body of liquid is a result of all the forces which act upon it. Larger quantities of liquid take the shape of the containers which hold them, and their shape is only slightly influenced by surface tension near the walls.

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[5] Pauling, L. C., *The Nature of the Chemical Bond*, p. 284 (1940).

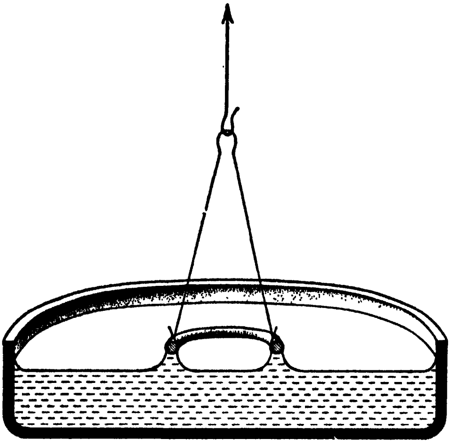

FIG. 3–4. A ring tensiometer showing the shape of the surface.

When the surface of a liquid is expanded, work must be done to pull molecules out into the new surface. This work is the free surface energy of the liquid and is expressed in units of ergs per square centimeter. Since work must be done to expand a liquid surface, the surface will exert a pull opposing any motion which produces a larger surface. This pull can be measured by placing a clean wire in the surface, where it will stick to the liquid, and pulling upward on it. Figure 3–4 shows the shape of a liquid surface which is being pulled up by a wire ring. The pull on the wire is opposed by the downward pull of two liquid surfaces, one on the inside and one on the outside of the ring. The maximum pull per centimeter which can be exerted by a liquid surface is called the surface tension, γ. The surface tension is expressed in units of dynes per centimeter.

It can easily be demonstrated that the surface energy and the surface tension are mathematically identical. The work necessary to pull out 1 cm^2 of new surface is equal to the pull on 1 cm of length, times the distance through which the pull is exerted, which is also 1 cm. The unit of surface energy, ergs per centimeter, is equal to dyne × cm per cm^2 or dyne per cm, which is the unit of surface tension. The surface tension of most organic liquids is of the order of 20 to 40 dyne per cm at room temperatures but water has a surface tension of 73 dyne per cm at 20° C. and molten metals have surface tensions which are greater than 400 dyne per cm. A pull of 1 dyne is approximately the pull of gravity of a weight of 1 mg (actually the pull on 1/980 of a gram).

Surface tension can be measured by the maximum pull necessary to remove a wire from the surface of a liquid. A convenient apparatus for this purpose was developed by du Nouy and is known as the du Nouy Tensiometer (Figure 3–5). In this instrument the pull is derived from a torsion wire which can be calibrated to read surface tension directly. An instrument of this type is subject to deviations from the simple theory, which states that the surface tension is equal to the observed pull divided by twice the circumference of the ring. These errors have been investigated by Harkins and Jordan[6] who have published tables of correction factors for various ring diameters and wire thicknesses. It would be a great convenience if commercially available rings were supplied with a table or graph of correction factors calculated for the dimension of the rings.

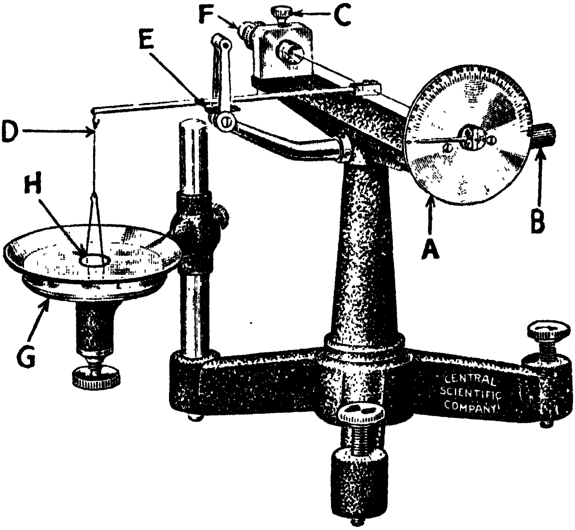

FIG. 3–5. The du Nouy Tensiometer. (Courtesy of the Central Scientific Co.)

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[6] Harkins, W. D., and Jordan, H. F., *J. Am. Chem. Soc.* **52,** 1751 (1930).

The pull of surface tension on a curved surface of a liquid produces a greater pressure inside the curve than exists outside. The difference in pressure, p, is inversely proportional to the radius of the curved surface. Consider a small drop of radius, r, and diameter, d, which is divided into two hemispheres by an imaginary plane. The pull of surface tension on the edge of the hemisphere is:

$$J = 2\pi\gamma r = \pi\gamma d. \qquad (3\text{–}3)$$

The force opposing this pull will be the pressure inside the drop times the area of the circle at the diameter.

$$J' = \pi r^2 p = \pi d^2 p/4. \qquad (3\text{–}4)$$

Since the force exerted by the pressure inside must exactly balance the pull due to surface tension, J must equal J', and we find that

$$p = 2\gamma/r \qquad \text{or} \qquad p = 4\gamma/d. \qquad (3\text{–}5)$$

The second form of equation 3–5 is useful for small spheres of fluid. The first form is more useful for surfaces which are not spherical, in which case r is the radius of curvature. (If the curvature is not the same in all directions, the equivalent radius is given by $1/r = 1/r' + 1/r''$ where r' and r'' are the maximum and minimum radii of curvature.)

If we measure the pressure inside a drop of liquid, or inside a bubble blown under the liquid, we can calculate the surface tension from the observed diameter of the bubble. The pressure inside bubbles of convenient size is quite small, however. For water, if the diameter is 1 cm, $p = 4 \times 73/1$, which is 292 dynes per cm^2. This is the pressure of a column of water about 3 mm high.

One very convenient modification of the direct method of measuring the pressure and the diameter of a bubble is known as the maximum bubble pressure method. A bubble which is being blown at the end of a tube has its minimum radius when it is a hemisphere with the same radius as the tube from which it is blown. The minimum radius corresponds to a maximum pressure which is directly proportional to the surface tension for any given tube.

Most liquids will wet glass because the molecules of the liquid are attracted to the glass more strongly than they are attracted to molecules of their own kind. When such a liquid is placed in a glass container it will rise along the container and will meet the wall at a tangent. If a small glass tube is placed in a liquid the liquid will rise inside the tube and the surface or meniscus of the liquid will be approximately a hemisphere (see Figure 3–6). The pressure above the liquid surface must be greater than in the liquid by $p = 4\gamma/d$, where d is the diameter of the capillary. Since the pressure above the liquid is atmospheric the liquid must rise in the capillary until its height, h, reduces the pressure on the liquid by an amount, p. The pressure of a column of liquid equals $h g \rho$, where ρ is the density and g is the gravitational constant. We therefore find that the surface tension, γ, is given by

$$\gamma = dhg\rho/4 \tag{3-6}$$

for a rise of h centimeters in a capillary with a diameter of d centimeters.

The surface tension can also be determined from the shape or size of a hanging drop. An early instrument for measuring the maximum size of hanging drops is the Ostwald stalagometer. This is a pipette with a carefully ground tip, and the pipette is filled with a measured quantity of liquid. The number of drops which fall from the tip is, as a first approximation, inversely proportional to the surface tension. This is only approximately true and the errors may be as great as 20% or 30%, even if the capillary is calibrated with a liquid of known surface tension. Harkins and Brown[7] have calculated the corrections which must be applied to measurements of surface tension by the drop weight method.

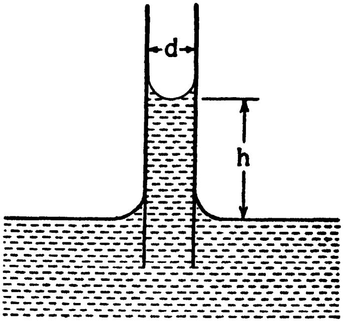

Fig. 3–6. The rise of a liquid in a capillary tube.

A very precise and reproducible method of measuring surface tension has been developed by Hauser and his students.[8] A hanging drop is photographed and the surface tension is calculated from the dimensions of the drop. Unfortunately, the calculations are indirect and the measurements do not appear to be simple. The hanging drop method is, however, superior to the capillary rise method for all systems which are subject to contamination, since a new surface can easily be produced if contamination is suspected.

Monomolecular Layers on Water.—If molecules of a hydrocarbon, such as octadecane $CH_3—(CH_2)_{16}—CH_3$, are placed on water, they will stay on top of the water and will collect into a small drop because the attractive forces between the water and the hydrocarbon molecules are less than that between two water molecules or two hydrocarbon molecules. If, instead of a hydrocarbon, we place molecules of stearic acid, $CH_3—(CH_2)_{16}—COOH$, on the surface, the —COOH groups will be strongly attracted to the water. The hydrocarbon part of the molecule is still insoluble in water, and thus the molecules will form a layer on top of the water. The polar heads of the stearic acid, the —COOH groups, will be in the water and the hydrocarbon chains will be in the air as is shown schematically in Figure 3–7.

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[7] Harkins, W. D., and Brown, R., *J. Am. Chem. Soc.* **41**, 499 (1919). See also Hauser and Lynn, *Experiments in Colloid Chemistry* (1940). Harkins, W. D., and Freud, B. B., *J. Phys. Chem.* **33**, 1217 (1929).

[8] Andreas, V. M., Hauser, E. A., and Tucker, W. B., *J. Phys. Chem.* **42**, 1001 (1938).

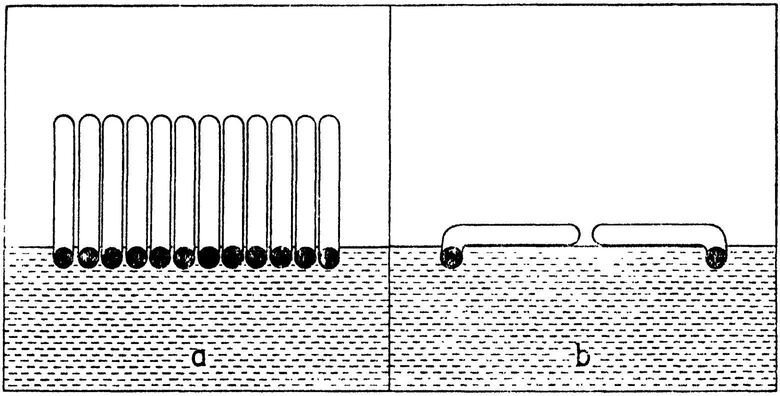

Fig. 3–7 a and b. Monolayers on water, a. condensed, b. expanded.

This layer will be only one molecule thick and there will be no tendency for another oriented layer of stearic acid to form on top of the first layer because there is no polar surface to orient an additional layer. Monomolecular layers, or surface layers which are one molecule thick, are called "monolayers" for short. If more stearic acid is put on a surface than can be accommodated in a monolayer, the rest will pile up as a crystal or thick lens, depending upon the temperature.

The surface tension of water is lowered by the presence of a monolayer on the surface. The polar groups exert an upward attractive force on the water molecules and balance some or all of the surface tension of the water. The hydrocarbon layer on top has a much lower surface tension, and the resultant surface tension is closer to the surface tension of an oil than to the surface tension of pure water.

If there is an insoluble surface active agent on the water (there need not be enough to cover the surface completely), the molecules of the surface active agent will be in continuous motion and will bombard, and exert a pressure upon the walls and other boundaries of the surface. This bombardment will be opposed to the surface tension and will reduce its magnitude. The foregoing is a kinetic interpretation of the lowering of the surface tension by surface impurities and has equal validity with the potential explanation of the same phenomenon in the preceding paragraph.

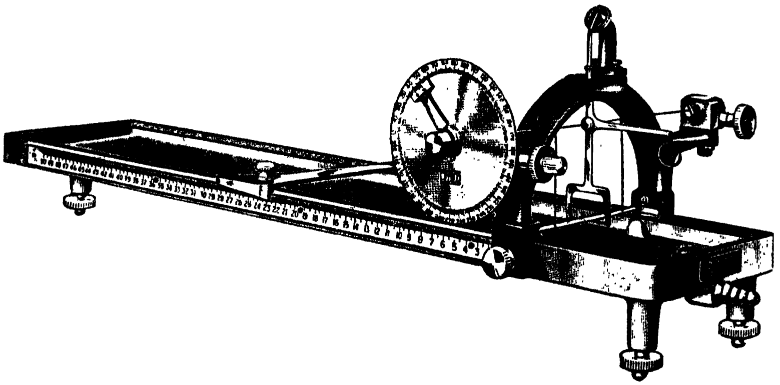

FIG. 3–8. Surface balance. (Courtesy of the Central Scientific Co.)

The pressure exerted on a line in the surface is called the surface pressure, σ. (Many authors call this quantity F and speak of it as a force.) The surface pressure, σ, is equal to the surface tension of a clean solution, γ_0, minus the surface tension of a contaminated solution, γ.

$$\gamma = \gamma_0 - \gamma. \tag{3–7}$$

The surface pressure can be measured by an ingenious device known as a surface balance which is the result of successive contributions from Miss Pockels, Irving Langmuir, and N. K. Adam (see Figure 3–8). Miss Pockels showed how it is possible to remove surface contaminations by pushing the impurities back with a barrier which extends all the way across a trough which is full to the brim with water. Langmuir found that the surface pressure could be measured by a floating barrier which is hung in the surface from a torsion wire.[9]

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[9] Langmuir's original apparatus made use of air jets to prevent leakage around the end of the float. N. K. Adam greatly improved the apparatus by substituting flexible vertical strips of gold foil to keep the surface layer on one side of the barrier. These gold strips can be replaced by Vaselined silk threads for all but the most exacting work.

The water on one side of the float is swept clean and the other, after sweeping, is contaminated with a known quantity of surface-active insoluble material. The float is pushed back by the surface pressure (or is pulled back by the difference in surface tension), and the force necessary to restore the float to its original position is the surface force. The surface pressure is equal to this force divided by the length of the float. The area of the surface layer can be altered by moving a barrier on the contaminated side of the float. A graph of the surface pressure as a function of the area, usually per molecule, gives a great deal of information about the surface layer, and is analogous to a graph of the pressure as a function of the volume of a three-dimensional system.

Substances which form monolayers include those organic substances which contain from about 12 to 40 carbon atoms and at least one group which is strongly attracted to water. Examples are the acids, alcohols, ketones, esters, amines, phenols, and amides. Almost any group which contains oxygen or nitrogen atoms will be attracted to water. The hydrocarbon portion of the molecule may have various configurations—straight or branched chains, or ring structures such as are found in cholesterol and many other sterols. The hydrocarbon portion must be large enough to prevent the hydrophilic group from pulling the whole molecule into the water. Organic anions and cations, such as $RCOO^-$ and RNH_3^+, are among the most hydrophilic groups known and a much longer hydrocarbon chain is required to keep these ionic groups on the surface. The insoluble salts of carboxylate ions with polyvalent metals, such as $(RCOO)_2Ca$, form excellent monolayers. These are usually prepared by spreading the corresponding acid on a dilute neutral or alkaline solution of the cation. The amount of heavy metal ions which are normally present in distilled water produce metal soaps when stearic acid is spread on the surface. A monolayer of stearic acid can be obtained only by spreading on a dilute solution of a mineral acid.

Figure 3–9 shows a diagram of surface pressure versus area per molecule for an idealized surface film. At very large areas per molecule, the molecules on the surface will behave as independent kinetic units and each one will exert a thrust on the barrier which is independent of the presence of other molecules. The monolayer will behave like a two-dimensional gas. If A is the area per mol, the product of the surface pressure and the area will be a constant.

$$\sigma A = RT. \tag{3–8}$$

This is the two-dimensional analog of the perfect gas law, $PV = RT$, where V is the volume occupied by 1 mol. All substances which have been experimentally studied begin to show deviations from equation 3–7 at surface pressures of a few tenths of a dyne per centimeter.

When a surface is covered with a monolayer, so that the molecules are just touching, a large increase in pressure will be required to produce a small change in surface area. This is represented in Figure 3–9 as the nearly vertical portion of the $\sigma - A$ curve. The area of this condensed film is a direct measure of the cross-sectional area of the molecules in the surface.

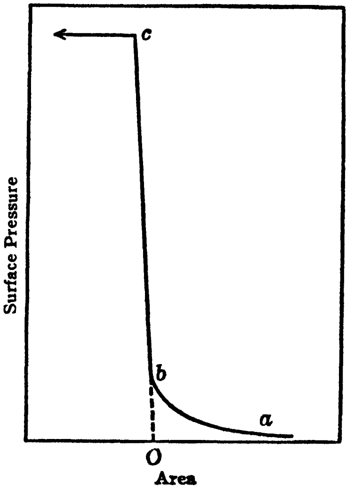

FIG. 3–9. Surface pressure and area of an idealized monolayer. (From Glasstone, *Textbook of Physical Chemistry*, 2nd Ed., Van Nostrand (1946).)

An experimental determination of the cross-sectional area of a stearic acid molecule might be carried out as follows. Two drops (0.1 ml) of a solution of stearic acid in benzene containing 0.0002 mol or 0.057 gm of acid per 100 ml of benzene is placed on a surface. The benzene evaporates leaving 0.000057 gm of stearic acid on the surface. This monolayer is compressed by a barrier until it is solid, and the pressure rises rapidly. The area of the condensed film is found to be 240 cm^2. The problem is to calculate the area per molecule. The number of molecules on the surface is $N \times 0.000057/M$, where N is Avogadro's number and M is the molecular weight of stearic acid —about 285. The number of molecules on the surface is therefore $6 \times 10^{23} \times 0.000057/285$ or 12×10^{16} and, since the total area is 240 cm^2, the area per molecule is approximately 20×10^{-16} cm^2 or 20 Å^2. The area of most straight chain molecules which have a single polar group at one end is 20.5 A^2 when the area of the condensed phase is extrapolated to zero pressure as shown in the dotted line in Figure 3–9.

At intermediate surface areas between the condensed phase, where the molecules are all standing up, and the gaseous phase, where all molecules are acting independently, there are a bewildering number of other phases. Reference should be made to N. K. Adam, *The Physics and Chemistry of Surfaces*, for an extensive review of the observed phenomena, and also to Harkins in *Alexander's Colloid Chemistry*, Vol. 5.

When the surface pressure on a monolayer of an oil is increased, the film eventually collapses to one or more small lenses. The surface pressure of the condensed film, which is in equilibrium with the lenses of oil, is constant and independent of the area, so long as there is excess oil on the surface. This provides a very convenient device for maintaining a constant surface pressure. The surface pressure can be transmitted to another film on the surface through a Vaselined thread "piston" which lies in the surface.

Multilayers.—Condensed monolayers on the surface of water will be transferred to the surface of a slide which is dipped through the surface. Some layers, notably barium stearate (a film of stearic acid spread on dilute barium chloride or barium hydroxide), will stick to the slide as it goes down and another layer will be deposited on the slide when it comes up again. Successive monolayers can be deposited in this way and it is possible to build up "multilayers" which are several thousand monolayers thick. The thickness of a barium stearate monolayer is about 24 Å, so this technique permits one to prepare films having a carefully controlled thickness in units of 24 Å. The layers recrystallize fairly rapidly and lose their initial lamellar structure, but the average thickness of the multilayer is not changed by this molecular migration and rearrangement.[10]

Soluble Surface-Active Agents.—Molecules which contain both a water-soluble and an oil-soluble group, and which are soluble in water, are concentrated at the surface of their aqueous solutions. These substances are known as surface-active agents. Any of the lower homologs of the monolayer-forming substances will be surface active. The oil-like end of a surface-active molecule will have little attraction for the water and there will be a tendency for it to accumulate in a surface layer. The molecules which are in the surface layer will exert a surface pressure and lower the surface tension in the same way that the molecules in a monolayer do. There is this difference, however. The surface tension will depend only upon the concentration. If we try to compress the surface layer by reducing the area, some of the molecules will be forced down into the solution.

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[10] Germer, L. H., and Storks, K. H., *J. Chem. Phys.* **6**, 280 (1938).

There are some transient effects which are noticed when the surface of a solution of a surface-active agent is expanded or compressed, because the surface-active molecules require a relatively long time to arrange themselves in the surface layer. This is most dramatically shown by measurements on the surface tension of fresh surfaces. Ordinary methods for measuring surface tension are relatively slow, but the surface tension can be calculated from the shape of a stream of water as it issues from an elliptical jet.[11] These measurements show that the surface tension of a new surface of sodium oleate is approximately the same as that of pure water, but that this value falls to about 25 dynes per cm as the oleate radicals migrate to the surface and form a monolayer. Some surface-active agents may require as much as a day before their surface tension reaches a steady value.

The most effective soluble surface-active agents have an ionic group as the water-soluble part of the molecule. Ions have a greater attraction for water than any other hydrophilic group, because the charge on the ion attracts water dipoles. This attractive force is so great that every ion in solution is surrounded by a shell of water molecules. Because of their great attraction for water, ions are capable of pulling long carbon chains into solution. Although oleic and stearic acids are quite insoluble in water, their ions, as sodium oleate and sodium stearate, are soluble. (Sodium stearate becomes appreciably soluble above 60° C.) Even in very dilute solutions these substances are concentrated on the surface and lower the surface tension of water to less than half of its original value. In more concentrated solutions the ionic surface active agents aggregate to form a class of colloids which are known as "colloidal electrolytes" (see Chapter 9).

There is a very large number of commercial surface active agents but they all have about the same effect on the surface tension of water.[12] Figure 3–10, taken from a recent conference on surface-active agents,[13] shows that the surface tension has reached its lowest value, between 25 and 40 dynes per cm at about 0.1% concentration,

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[11] Adam, N. K., *The Physics and Chemistry of Surfaces*, 3rd Ed., p. 386 (1941).

[12] See Flett, L. H., *Alexander's Colloid Chemistry* 6, 243 (1946).

[13] *Annals of the New York Academy of Sciences* **46**, No. 6, 347–530 (1946).

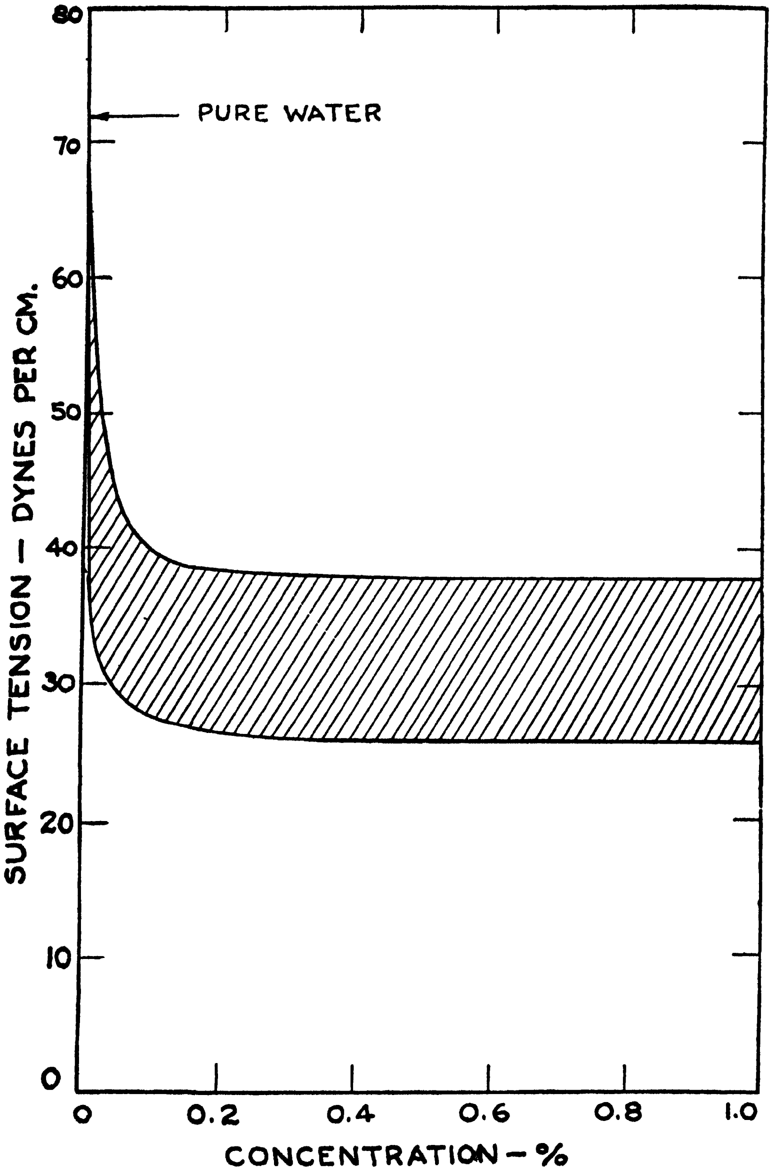

FIG. 3–10. Surface tension of commercial surface active agents. (From Fisher and Gans, *Annals of the New York Academy of Sciences* 46 (1946).)

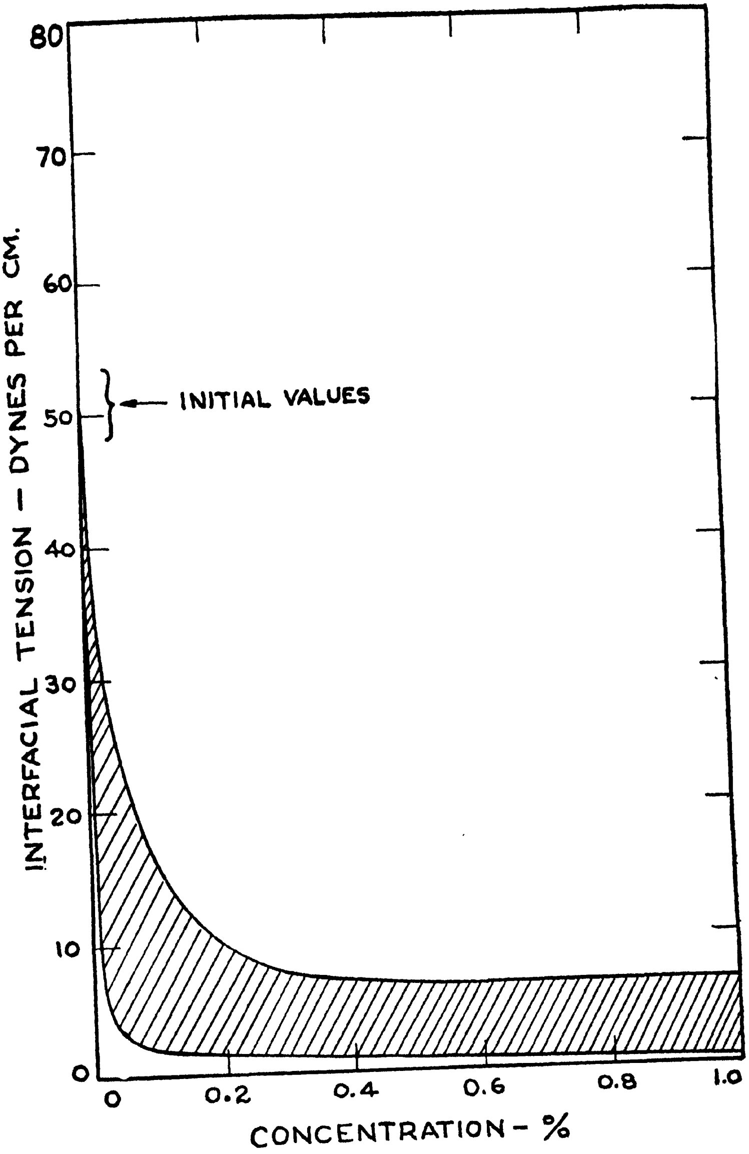

FIG. 3-11. Interfacial tensions (water against oils) of commercial surface active agents. (From Fisher and Gans, *Annals of the New York Academy of Sciences* (1946).)

and that the surface tension is nearly independent of the concentration of the surface active agent above 0.2%.

The Adhesion of Liquids to Other Surfaces.—A molecule of water at the interface between water and an oil will be attracted more strongly by water molecules than by oil molecules. This unequal attraction will give rise to an interfacial tension similar in many respects to the surface tension. Since oil molecules do have some van der Waals forces of attraction for water molecules, the interfacial tension will not be as great as the surface tension of pure water. The interfacial tension of most non-surface-active oils against water lies between 30 and 50 dynes per cm. Oils which contain hydrophilic groups have much lower interfacial tensions, as might be expected. The effect of surface-active agents on the interfacial tension is shown in Figure 3–11. Most agents lower the interfacial tension to very low values at concentrations of 0.1%. This is to be expected because the molecules of the surface active agent which are oriented in the interface have an attraction of water on one side and an attraction for oil on the other side. Some branched-chain surface active agents will lower the interfacial tension to 0.05 dyne per cm.

When a small drop of an oil is placed on water it will remain as a lens unless the molecules of the oil have a stronger attraction for water than they have for themselves. When an oil spreads on water the free surface of the oil is increased and the free surface of the water is decreased. The interfacial area between the oil and the water is also increased. If we represent by γ_0 the surface energy of the water, by γ_1 the surface energy of the oil, and by γ_{01} the interfacial energy, then the work which must be done to produce spreading is

$$W_s = \gamma_1 + \gamma_{01} - \gamma_0 \tag{3–9}$$

If the work of spreading is negative, the oil will spread spontaneously.

The spreading of a liquid on a solid surface is subject to the same conditions which apply to the spreading of an oil on the surface of water. Although it is impossible to measure either the surface tension, γ_s, or the interfacial tension, γ_{0s}, of a solid surface, the difference $(\gamma_s - \gamma_{0s})$ can be measured because it is equal to the free energy of immersion of the solid. When a solid particle is completely immersed in a liquid, the surface energy against air, γ_s, is replaced by the interfacial energy against the immersion liquid, γ_{0s}, and this change in surface energy can be measured in a calorimeter. The actual values are very small and it is only possible to measure the energy of immersion for powders which have a large surface area per gram.

When a drop of water, or other liquid, is placed on a solid surface, it may stand up as a drop or it may flow out and wet the surface. If the molecules of the liquid are attracted more strongly to the solid than to each other, the liquid will spread on the surface and there will be no contact angle. If the molecular cohesion in the liquid exceeds the adhesion of the liquid for the solid, there will be an angle of contact, Θ, between the liquid and the solid (see Figure 3–12). Water and most simple liquids have zero contact angles on clean glass and on most clean metals. The contact angle of water on paraffin surfaces is 105°, and mercury on steel (actually on a surface layer of iron oxide) is reported to have a contact angle of 154°.[14] A contact angle of 180° would imply no attractive forces whatsoever between the molecules of the liquid and those of the solid. No substances show this behavior and therefore any liquid will wet any solid to some extent. It has been customary to say that a liquid which has a contact angle greater than 90° on a solid does not wet the solid, and that one with a contact angle less than 90° does wet it. It might be better to say that a solid is incompletely wet by a liquid if there is a contact angle other than zero. Although water does not appear to wet a paraffin surface, it is easy to demonstrate that there is a force of attraction between water and a paraffin surface. Small drops of water on a block of paraffin will not fall off if the surface is inverted. They are held on against the pull of gravity only by the attractive forces between the water and the paraffin.

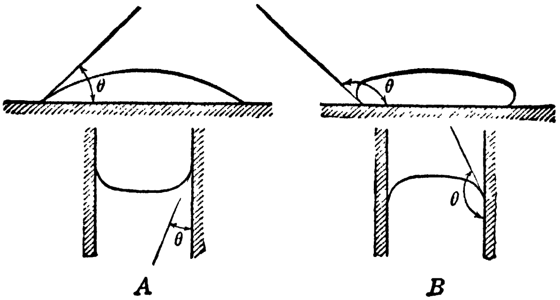

Fig. 3–12. Contact angles. (From Glasstone, *Textbook of Physical Chemistry*, 2nd Ed., Van Nostrand (1946).)

It is very difficult to obtain reproducible values for the contact angle, although it is relatively easy to measure the contact angle in any given instance. The lack of reproducibility may be traced to the state of the solid surface. As a liquid drop advances over a surface it comes in contact with a dry surface. As the drop leaves a surface it leaves it covered with a thin layer of molecules of the liquid. Under these conditions the advancing and receding contact angles will not be the same and, in general, the advancing contact angle will be the greater. The shape of drops of water as they roll down a window pane is to be accounted for in this way. Reproducible contact angles can only be obtained if the surface is first brought into equilibrium with the saturated vapor of the liquid whose contact angle is being measured.[15] This is essentially the same as saying that only receding contact angles represent equilibrium conditions.

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[14] Adam, N. K., *The Physics and Chemistry of Surfaces*, 3rd Ed., p. 186 (1941).

Wetting and Spreading.—Surface-active agents lower both the surface tension of a liquid, γ_0, and the interfacial tension of a liquid for a solid, γ_{0s}. The energy necessary to produce spreading is equal to the sum of these two surface energies minus the surface energy of the solid, γ_s.

$$W_s = \gamma_0 + \gamma_{0s} - \gamma_s. \tag{3-10}$$

This equation is identical in form with equation 3–9 for the spreading of one liquid on another. The most important action of "wetting agents" is probably to reduce the interfacial tension, γ_{0s}, although the reduction in γ_0 is also important. The best wetting agents are those which produce the lowest interfacial tensions against oils. The surface tension of a solution of a good wetting agent is nearly the same as the surface tension of a poor wetting agent.

A fabric can be made "shower-proof" by applying to the surface of each fiber a substance which has a high contact angle against water. If the contact angle could be made 180°, the pressure necessary to force water through a hole of diameter, d, would be given by equation 3–5 as

$$p = 4\,\gamma/d. \tag{3-5a}$$

Contact angles of 180° are never found and the pressure necessary to force a liquid through a hole when there is a contact angle is

$$p = -4\gamma\cos\Theta/d. \tag{3-11}$$

This same law applies to the capillary rise of a liquid which wets the tube incompletely, if you substitute the height and density of the liquid for the pressure. Mercury has a contact angle on glass which is 140°. The cosine of 140° is a negative quantity and, as a result, mercury does not rise in capillary tubes but is depressed. The surface tension of mercury is high and therefore considerable pressure is required to blow or suck mercury into a capillary tube. It is difficult to handle mercury in an ordinary pipette for this reason.

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[15] MacDougall, G., and Okrent, C., *Proc. Roy. Soc. London* **A 180**, 151 (1942).

The zero contact angle of water on wet fabrics means a contact angle of 180° for air against wet fabric. This means that a wet fabric will hold air until the pressure reaches a value which may be calculated from equation 3–5. This principle has been applied in the construction of water-wings, which will hold air when they are wet.

Aquatic birds obtain their buoyancy from the air in their feathers. The high contact angle of water on their feathers keeps water from penetrating; and the air, which is contained in the porous feather structure, keeps the bird afloat. A good wetting agent will therefore sink a duck (this was an impressive although perhaps cruel publicity demonstration a few years ago). The duck sinks because the contact angle of water on its feathers is reduced below 90°, and water displaces the air which kept it afloat.

Although it may be cruel to sink a live duck with a wetting agent, you can use one of these agents to advantage on dead ducks and geese. Bird feathers can easily be removed if you can get scalding water onto the base of the feathers. An edible wetting agent or even a solution of tri-sodium phosphate, will permit the scalding water to wet and penetrate to the base of the feathers of a duck. Plucking a properly scalded duck is then no more trouble than plucking a chicken.

Wetting agents have very important applications in the field of textiles and in other fields where finely divided dry materials must be rapidly wet. These agents do not, however, make any appreciable difference in the rate of penetration of liquids into material which is already wet. Therefore they would not be expected to improve the penetration of histological fixatives and stains. Wetting agents can greatly improve the adhesion of agricultural sprays to the leaves of plants, because most leaves are not completely wet by water or salt solutions. Wetting agents improve the coverage by permitting the drops to spread out and cover a larger part of the leaf. They also reduce the loss of drops which will roll off an imperfectly wet leaf. Not all wetting agents can be used with any given spray. It is necessary to consider the chemical reactivity of the constituents of the spray. For example, copper ions will precipitate ordinary soaps, and very few anionic reagents can be used in solutions of heavy metal ions. The choice of a wetting agent for a given application is similar to the choice of a soap or detergent. For a further discussion of this subject see Chapter 9 on colloidal electrolytes, page 222.

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CHAPTER 4

ADSORPTION

Definitions.—Nearly all surfaces have attractive forces for molecules of gases or solutes and will concentrate these substances on their surfaces. This process is called "adsorption." Adsorption is primarily a colloidal phenomenon because only in colloids do we find material with sufficient surface area to adsorb appreciable quantities of other substances. The term "*ab*sorption" is used to designate the uptake of a substance, or radiant energy, inside the structure of a solid or liquid. There is little or no distinction between *ab*sorption and solution of molecules. Although it is easy to define the difference between adsorption and solution it is frequently very difficult to distinguish the two phenomena in practice. For this reason McBain, in 1909, suggested the term "sorption" to cover both *ab*- and ad-sorption. The term sorption will be used in this book wherever there is no definite indication that the phenomena are due solely to adsorption. Most of the theoretical considerations deal with adsorption and will be so designated.

On a molecular level there can be little distinction between *ab*sorption and adsorption, by highly porous solids. Some solids are so porous that nearly all of the atoms can come in contact with the molecules of a gas. Such a solid is chabazite, one of the silicate minerals. The pores of this mineral are about 4.5 Å in diameter and it becomes extremely difficult to decide whether they adsorb or *ab*sorb a gas.[1] In either case the gas is held by the attraction of the atoms with which it is in contact, and any distinction between *ab*- and ad-sorption ultimately rests on our definition of what we mean by inside. It has been usual to consider that the surface of a hole through a solid is outside the material of the solid. We use the same definition of outside when we say that a person in a large courtyard surrounded by a building is outside and not inside the building.

Sorption on solid surfaces, which is usually adsorption, plays a very important role in colloid chemistry. The surfaces of most colloids are covered with an adsorbed layer which determines their properties. As a practical tool, sorption is one of the most economical, and sometimes the only feasible, method for removing impurities in industrial processes. The ability of charcoal to adsorb all large vapor molecules is made use of in gas masks and in solvent recovery systems. Sorbents are used to decolorize or deodorize a wide variety of products including sugar, lubricating oil and drinking water. The recovery of penicillin from very dilute solutions in culture media makes use of adsorption on charcoal at one stage.[2] Sorption holds the dye on our clothes as well as the stains used on histological specimens. The adsorption of impurities on precipitates is of importance to the analytical chemist, and the farmer depends upon sorption to hold the fertilizer in the soil until it is needed by the plants.

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[1] McBain, J. W., calls this example persorption. *Trans. Faraday Soc.* **28**, 408 (1932).

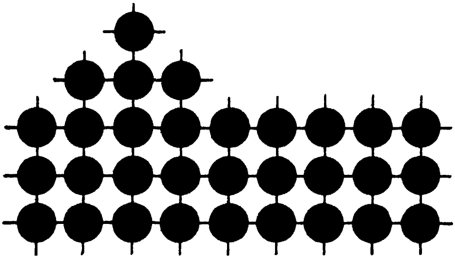

FIG. 4–1. Unsatisfied bonds at the edges and faces of a cubic crystal.

The Forces Which Cause Adsorption.—We have seen in the previous chapter that the atoms and molecules at the surface of a body have unbalanced attractive forces. An atom at the surface of a solid or liquid will attract any other atom which comes in contact with it. The attractive force will, of course, depend upon the nature of the molecules concerned, but it will usually be intermediate between the intermolecular forces of the two substances which are in contact.

The attractive forces at the surface of a liquid are, on the average, identical over the entire surface because the molecules are free to adjust themselves until they all occupy equivalent positions. In a solid the molecules at a corner or edge of a crystal will have more "unsatisfied bonds" than molecules in the middle of a surface. Figure 4–1 represents the free forces of molecules on the surface and on the edge of a cubic crystal. These forces will attract molecules of the same kind, if any are available, and the crystal may grow if the rate of evaporation is less than the rate of condensation.

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[2] Helbig, W. A., *Alexander's Colloid Chemistry* 6, 1176 (1946).

When foreign molecules come in contact with molecules on a surface, they will also be attracted and will stick until they obtain sufficient thermal energy to evaporate. The molecules of the vapor of a liquid with a high boiling point have greater intermolecular attractive forces than the molecules of a gas or vapor of a low boiling liquid. We would therefore expect to find that adsorption increases with an increase in boiling point. This is found to be the case experimentally for all adsorbents with pores large enough to admit the larger vapor molecules.

Chemical similarities between the sorbent and the sorbate (that which is sorbed) also influence the extent of sorption. Water is strongly adsorbed on silica because it can enter the coordination shell of the peripheral silicon atoms and can also form hydrogen bonds with the available oxygen atoms (see Chapter 11). Charcoal, which is porous carbon, has a graphite structure resembling the aromatic hydrocarbons and, as might be expected, adsorbs benzene and other organic vapors much more strongly than it adsorbs water. In general, we can say that polar mineral adsorbents and organic substances, which have many —OH groups such as starch and cellulose, will preferentially adsorb water and polar vapors, whereas organic vapors will be more strongly adsorbed on non-polar adsorbents of which charcoal is the outstanding example.

Adsorption from solution follows laws very similar to those which govern adsorption from gases and vapors, but there is the added complication that the solvent is also adsorbed. As a result, adsorption from solution always involves displacement and the effects are correspondingly more complicated. For example, if the solvent is adsorbed more strongly than the solute, the remainder of the solution will become more concentrated and adsorption of the solute will therefore be negative. When ions are present in solution and on the adsorbent, the effects produced by the ions will dominate the picture. For this reason ionic adsorption is discussed separately in the following chapter.

Types of Adsorbed Layers.—We have already discussed one type of adsorbed layer in Chapter 3; this is the monomolecular layer or monolayer. Monolayers are apparently the only stable type of adsorbed layer on the surface of water. All experiments indicate that thicker films eventually break up into one or more thick regions in equilibrium with a monolayer.

Monolayers of adsorbed substances will form on solids under several conditions, some of which precede the formation of thicker film. When the molecules of the substance which is being adsorbed have little attraction for each other, as in the case of a gas, the adsorption will cease when the surface is covered with a layer one molecule thick. There is little intermolecular attraction between gas molecules, and when they cover the surface of a solid with a monolayer they effectively insulate other molecules from the attractive forces of the solid underneath. This is a direct consequence of that fact that most intermolecular forces fall off as the seventh power of the distance between centers and, as we saw in Chapter 3, the intermolecular forces are reduced to less than 1% of their value when the distance is doubled.

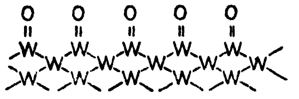

FIG. 4–2. A monolayer of chemically adsorbed oxygen on tungsten.

Monolayers will also be formed when the adsorbed substance reacts chemically with the molecules on the surface of the adsorbent. Langmuir found that oxygen is taken up by the surface of tungsten to form a surface oxide which is shown diagrammatically in Figure 4–2. The oxygen atoms are bound to the tungsten by strictly covalent chemical bonds and there is no reason to expect another layer of oxygen to be chemically adsorbed on top of the first.

Monolayers are also formed on some finely porous substances, such as chabazite, charcoal and some silica gels, if the pores are too small to allow more than one layer of adsorbed material. There has been a strong tendency to regard monolayer adsorption as the only possible case and to discount all possibility of multilayer sorption (except as capillary sorption (see next page). This represents an oversimplification of the facts since the majority of adsorbents will adsorb multimolecular layers of gases at low temperatures.

Multimolecular layers of adsorbed material will form if the adsorbed molecules have sufficient intermolecular attractive forces. This will be true for vapors; that is, gases below their critical point, and gases not too far above the critical point. Multilayers up to 16 molecules thick have been demonstrated, but it is unusual to find more than two or three adsorbed layers unless the vapor is very close to its saturation pressure. At the saturation pressure any number of layers is possible because the vapor will be in equilibrium with any amount of the liquid phase.

A liquid which wets a capillary pore is under tension for the same reason that a liquid rises in a capillary tube. This tension, or reduction in pressure on the liquid, is caused by the forces of surface tension acting on the curved meniscus in the pore. It has the same value as the pressure necessary to force air through a pore in a wet membrane (equation 3–11, p. 64).

The tension on the liquid in a capillary reduces the vapor pressure of the liquid just as the osmotic pressure increases the vapor pressure of a solution (page 40). This means that a liquid in a capillary will have a lower vapor pressure than a liquid with a plane surface. It also follows that the liquid in a capillary will not evaporate until the vapor pressure has dropped below the saturation pressure. Sufficiently small capillaries will therefore hold water vapor, for example, and may be said to adsorb the vapor. The equation which relates the relative vapor pressure in a capillary full of liquid to the diameter of the capillary and the surface tension of the liquid was first derived by Lord Kelvin.

$$ln\, p/p_0 = 4\gamma M/RT\rho d. \qquad (4\text{–}1)$$

In this equation $ln\, p/p_0$ is the natural logarithm of the ratio of the vapor pressure in the capillary, p, to the pressure of saturated vapor, p_0. The other symbols have the same meaning as in Chapters 2 and 3. (See the appendix of symbols.) For water at 20° C., 90% saturation occurs in pores 200 Å in diameter, and 50% saturation requires pores 29 Å in diameter. There is little doubt that capillary condensation does contribute to adsorption on solids like silica gel but, at low saturation pressures, it cannot explain the quantitative relationships since the required pores would be much smaller than a single molecule; nor can capillary condensation explain adsorption on plane surfaces.

Isotherms.—A graph of the quantity of material sorbed against the pressure or concentration of the sorbed material in equilibrium with the sorbent is called an isotherm. The word isotherm is derived from two Greek roots, *iso* meaning equal and *therm* which means heat or temperature. An isotherm is a plot of equilibrium conditions at constant temperature.

An isotherm of an adsorbed material is usually a curved line but it is worth while considering first two elementary cases which do not involve adsorption. If we have a bottle containing carbon tetrachloride and water and add iodine to this system the concentration of iodine in the carbon tetrachloride will always be greater than in the water, but the ratio of the two concentrations will be constant. A graph of the grams of iodine in 1 gm of carbon tetrachloride as a function of the concentration of iodine in the water will be a straight line. Figure 4–3a shows the isotherm for this system where the uptake is entirely accounted for by solution or *ab*sorption in the carbon tetrachloride layer.

The isotherm of a heterogeneous chemical reaction—for example, the formation of a hydrate—is quite different. If we expose $CaCl_2$ to water vapor, it will take up the water to form a monohydrate if the relative humidity is greater than 1.5% (0.3 mm Hg at 20° C.). If the water vapor pressure falls below 0.3 mm, the $CaCl_2 \cdot H_2O$ will decompose, liberating water to the atmosphere. If the relative humidity is increased to 5%, the $CaCl_2 \cdot H_2O$ will add another molecule of water; and at 22% relative humidity, the hexahydrate, $CaCl_2 \cdot 6\,H_2O$, will form. Figure 4–3b shows the isotherm of water vapor on calcium chloride at 20° C. It consists of a series of steps, at which the composition is independent of vapor pressure, separated by vertical portions where the composition changes at constant vapor pressure.

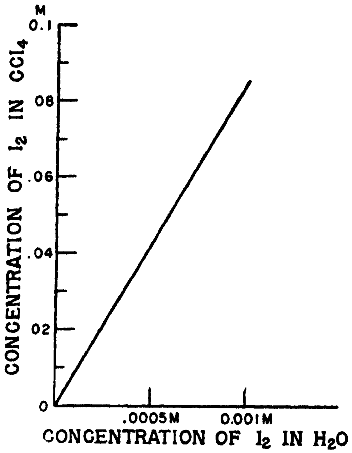

FIG. 4–3a. Isotherm of I_2 in CCl_4. (Solution)

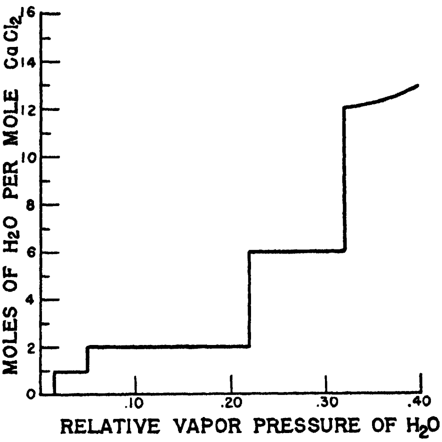

FIG. 4–3b. Isotherm of H_2O on $CaCl_2$. (Chemical Reaction)

A typical adsorption isotherm is shown in Figure 4–4 for the uptake of nitrogen gas on mica at 90° K (−183° C.). This isotherm is curved and there is no indication of the formation of a chemical compound at any pressure, and neither solution nor compound formation would be expected in this system. The shape of this isotherm is considered typical and is shown as a Type I or monolayer isotherm. There are two things which should be noticed about this isotherm. First, that most of the adsorption takes place at low pressures; and second, that adsorption appears to reach a maximum at high pressures.

The adsorption of vapors frequently follows an isotherm similar to a Type I isotherm at low pressures but at high relative pressures the adsorption increases again. This is known as a Type II or multilayer isotherm. Figure 4–5 shows the five principal types of isotherms which have been found.

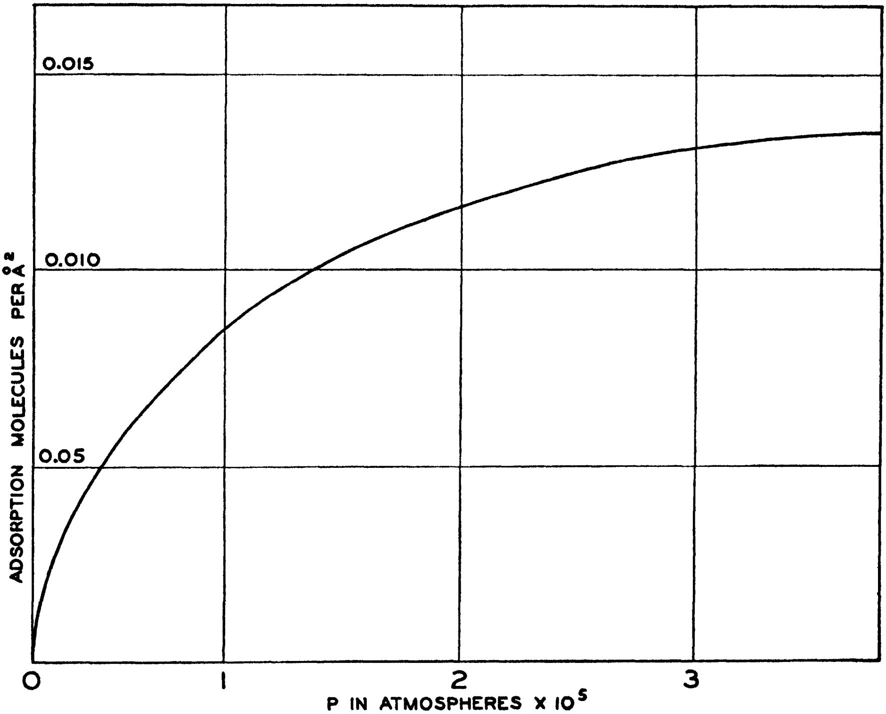

FIG. 4–4. The adsorption of nitrogen on mica at 90° A. (From data by Longman.)

Type I, or the monolayer adsorption isotherm, is obeyed when only one molecular layer is formed on the surface. Type II is typical of adsorption of gases such as N_2, A, O_2, CO_2, etc., at low temperatures on most substances except charcoal and chabazite. The upward swing of the isotherm at high pressures represents the formation of additional layers. Type III isotherms are found when the vapor molecules have greater attraction for each other than for the adsorbent. Monolayers are not formed with Type III or V isotherms; the first adsorbed molecules aggregate together into clusters. An example of a Type III isotherm is that of bromine vapor or silica gel. Isotherms of Types IV and V are found with those porous substances whose pores fill up before the saturation pressure is reached. Benzene on ferric oxide gel gives an isotherm of Type IV; and water on charcoal gives a Type V isotherm.[3]

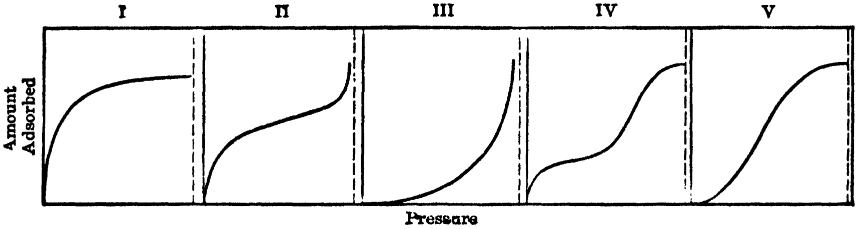

FIG. 4-5. Types of van der Waals' adsorption. (From Glasstone, *Textbook of Physical Chemistry*, 2nd Ed., Van Nostrand (1946).)

Methods for Measuring Sorption.—Sorption can be measured by a number of different methods which may be divided into two main types. The direct method is to measure the increase in weight of the sorbent or, in some cases, the quantity of sorbed material which can be removed from the sorbent after sorption is complete. The indirect method, which is the most common, is to measure the change in pressure or concentration of the sorbate and calculate from this change how much material has been sorbed.

An example of the direct method is given by the determination of the amount of sorbed water on wheat flour. The flour is weighed when it is in equilibrium with the moisture of the air; then the moisture is removed by heating to "constant weight." The difference in weight represents the sorbed water. The indirect method is exemplified by the measurement of the decolorizing power of charcoal. A weighed quantity of charcoal is shaken with a measured volume of colored solution. The charcoal is then filtered off and the concentration of the filtrate estimated by colorimetric methods. The amount sorbed is the difference between the initial and final concentrations times the volume of the fluid used.

Adsorption depends upon the surface area of the adsorbent and the quantities involved are extremely small. If a layer of molecules 10 Å (10^{-7} cm) thick is adsorbed on one square meter (10^4 cm^2) of surface the volume of adsorbed material will be only 10^{-3} cm³. One milligram of a material with a density of unity would therefore cover 1 square meter of surface. Egg albumin spreads to a layer nearly 10 Å thick on water and 1 gm could therefore cover a swimming-pool 10 meters wide and 100 meters long. It should be obvious that it will be impossible to weigh the material adsorbed on plane surfaces small enough to put inside a balance case unless the adsorbent is extremely thin.

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[3] Brunauer, S., *The Adsorption of Gases and Vapors*, Vol. 1, pp. 1–20 and pp. 149 150 (1943).

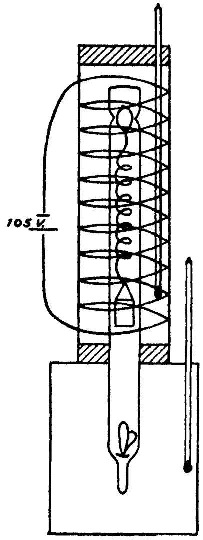

Fig. 4–6. McBain-Bakr sorption balance. (From Brunauer, *The Adsorption of Gases and Vapors*, Vol. 1, Princeton University Press (1943).)

Porous substances may have a very large surface area, up to several hundred square meters per gram, and these substances, whose pores are of colloidal dimensions, are the sorbents which have been most frequently studied. Finely divided powders will also have large surface areas and they have the added advantage, from a theoretical point of view, that their surface area can be computed from the dimensions of electron microscope photographs.

Although it would be theoretically desirable to express adsorption isotherms in terms of the surface area of the adsorbent, most adsorbents have unknown surface areas. Sorption is therefore usually expressed in terms of x/m, where x is the amount of material sorbed and m is the weight of the sorbent. The amount of sorption, x, may be expressed in any convenient units: for example, color, volume of gas, volume of gas reduced to a liquid, or most usually the weight of sorbed material. The values of x/m, when both are expressed in weight units, will vary from very low values on poor sorbents up to about 1.0 on the very best sorbents. Mantell[4] quotes data on a gas adsorbing carbon which held 110.9 gm of CCl_4 per 100 gm of carbon. This is an exceptionally high value and very few sorbents show x/m values greater than 0.5.

There are several special devices designed to measure the sorption of gases and vapors. Those designed to measure the residual gas pressure after sorption has taken place are usually very complicated. One of the simplest and most convenient methods of measuring the sorption of vapors is the McBain-Bakr sorption balance, Figure 4–6. This apparatus consists of a helical quartz fiber used as a Jolly balance to support a small platinum bucket containing the sorbent. The weight of the bucket and its contents can be calculated from the length of the spring, which in turn can be measured very accurately by a cathetometer. The vapor pressure can be changed by varying the temperature of the lower half of the chamber which contains liquid sorbate. The pressure in the upper half will equal the vapor pressure of the liquid in the coolest part of the tube. With this apparatus it is possible to seal up the sorbent and the sorbate and cover the complete range of pressure without opening the apparatus.

One practical method of measuring sorption is applicable to columns or tanks packed with the sorbent. For example, air containing a noxious vapor may be passed through a column of sorbent until the vapor is detected in the effluent. The volume of gas which is freed of vapor is a measure of the total capacity of the sorbent.

Theoretical Adsorption Isotherms.—Irving Langmuir developed one of the most successful equations for representing adsorption isotherms of Type I. The theory of the Langmuir isotherm is based on the following simple assumptions.

1. A molecule of a gas which strikes a surface will stick and evaporate after spending an average time, t, on the surface.
2. A molecule of gas which strikes an adsorbed gas molecule will be reflected.
3. The rate of evaporation from the surface is proportional to the fraction of the surface which is covered. (This is another way of saying that each molecule evaporates independently.)

The Langmuir adsorption isotherm can be expressed as:

$$x/m = abP/(1 + aP) \tag{4–2}$$

or

$$P/(x/m) = 1/ab + P/b. \tag{4–3}$$

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[4] *Adsorption*, p. 162 (1945).

The *a* term in the Langmuir isotherm is a multiplier of the pressure. A large value of *a* means that sorption will approach completion at low pressures and the isotherm will have a sharp corner. The *b* term multiplies the whole expression and at high pressures x/m will be proportional to *b*. An adsorbent which follows an isotherm with a large *b* term will have a large capacity. Figure 4–7 shows four Langmuir isotherms with different values of *a* and *b*. High values of *a* are usually associated with very strong adsorption energies such as are found in chemical adsorption, and in van der Waals' adsorption of large flat molecules which have many points of contact with the adsorbent. High values of *b* mean that the adsorbent has a large surface area.

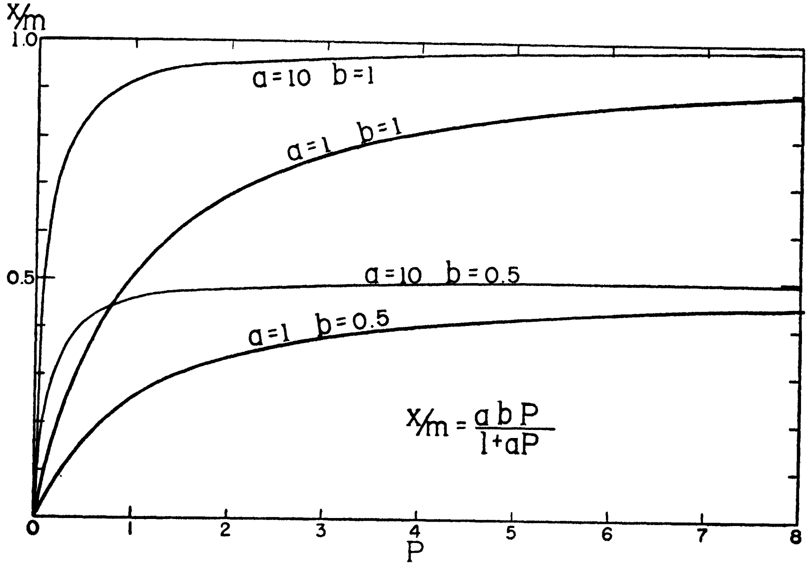

FIG. 4–7. Representative Langmuir isotherms.

The Langmuir isotherm can be derived as follows. Let ϕ be the fraction of the surface which is covered. The rate of evaporation, R, equals $c\phi$, where c is a constant. The rate of condensation, R', will be proportional to the pressure, P, and the fraction of the surface which is not covered $(1 - \phi)$. Therefore we can write

$$R' = kP(1 - \phi) \qquad (4\text{–}4)$$

where k is another constant. At equilibrium the rates of evaporation and condensation are equal and, therefore,

$$c\phi = kP(1 - \phi). \tag{4-5}$$

Solving for ϕ we find

$$\phi\,(c + kP) = kP \tag{4-6}$$

or

$$\phi = kP/(c + kP). \tag{4-7}$$

Now the quantity adsorbed is proportional to ϕ times the total surface area. We can, therefore, write

$$x/m = b\phi \tag{4-8}$$

where b is a constant proportional to the surface area. Both k and c are constants and we can express their quotient, k/c, by another constant, a. When we divide the numerator and denominator of the right-hand side of equation 4–7 by c and substitute a for k/c and $(x/m)/b$ for ϕ, we obtain the Langmuir isotherm,

$$x/m = abP/(1 + aP). \tag{4-2}$$

The Langmuir isotherm in its simple form is applicable only to adsorbed monolayers. There have been many attempts to extend the theory to multilayer adsorption and the most successful of these is the theory of Brunauer, Emmett, and Teller which is frequently referred to as The B.E.T. equation.[5] See also references by these authors at the end of this chapter. Harkins and Jura[6] have also studied the adsorption of successive layers of adsorbed vapors near the saturation pressure and have found evidence for as many as 12 adsorbed layers in some cases.

The B.E.T. theory is applicable only to the adsorption of vapors and can be written as

$$v = \frac{v_m\, cP}{(P_0 - P)\,[1 + (c - 1)\,(P/P_0)]}. \tag{4-9}$$

In this equation v is the volume the adsorbed vapor would have if it were compressed to a liquid. The volume of the adsorbed molecules which would cover the surface with a monolayer is v_m; P_0 is the saturation pressure of the vapor and P is the pressure at which the adsorption is measured. The constant term, c, is a measure of the relative magnitude of the forces between the adsorbed molecules, and the forces between the adsorbent and the adsorbed molecules. Equation 4–9 is derived for adsorption on plane surfaces where there is room for an infinite number of adsorbed layers. There are modifications of the B.E.T. equation for any finite number of layers but these equations have an extra constant.

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[5] Emmett, P. H., *Ind. and Eng. Chem.* **37**, 639 (1945).

[6] Harkins, W. D., and Jura, G., *J. Am. Chem. Soc.* **66**, 919, 1356, 1362, 1366 (1944).

The simple B.E.T. isotherm is most useful for predicting the surface area of solids from the quantity of gas which is adsorbed on the surface. The Langmuir isotherm can also be used for this purpose for those substances which form only monomolecular layers.

It is easy to calculate the surface area of a solid which obeys the Langmuir isotherm if we can estimate the area occupied by one molecule of the adsorbed substance. By equation 4–8, b equals x/m when the surface is saturated, and ϕ equals 1. If we know the area covered by one gram of the adsorbed material the surface area will be b times this area. This method has been used in the past with dyes which are very strongly adsorbed. Unfortunately many surfaces appear to adsorb dyes on only a small fraction of their area, probably on active spots. Although we cannot depend upon the absolute values of surface area which are determined by the adsorption of dyes, this method frequently gives very useful comparative values.

It should be obvious that the surface area of a porous substance depends upon the size of the measuring stick, which is of course the adsorbed molecule. Hydrogen molecules can enter pores and cracks which a nitrogen molecule could not penetrate; and nitrogen molecules can find more surface area than the large molecules of a dye. If we are going to use a charcoal for decolorizing, it is not sensible to measure its surface area by nitrogen adsorption. The measurement that will be most useful is its adsorptive capacity for the coloring matter it will have to remove.

Harkins and Jura[7] have developed a direct method for the measurement of surface area, based on the fact that some powders will adsorb water on their surface of such thickness that the surface energy of water on the particles is the same as the surface energy of bulk water. The heat liberated when the powder is immersed in water is a direct measure of the free-surface energy, and, by knowing the surface energy per square centimeter (it is numerically the same as the surface tension), they calculate the surface area.

The Freundlich Sorption Isotherm.—The so-called Freundlich or exponential isotherm is a purely empirical representation of sorption at intermediate pressures or concentrations. This isotherm is attributed to Boedecker but became generally known because Freundlich used it in his book, *Kapillarchemie* (Colloid and Capillary Chemistry). The isotherm takes the form,

$$x/m = kc^{1/n} \qquad \text{or} \qquad x/m = kP^{1/n} \tag{4–10}$$

depending upon whether sorption is from solution, where c represents the concentration in equilibrium with the sorbent; or from a gas, where P is the equilibrium pressure of the gas. A large value of n in the Freundlich (or exponential) isotherm means a very sharp corner and very strong sorption. The lower limit is $n = 1$, which is Henry's law for true solution. The constant, k, is proportional to the amount sorbed when c, or P, equals one. Neither of the constants in this isotherm have any theoretical significance but the curve does fit a large body of data with satisfactory accuracy and it is a very convenient form to handle graphically. In the form,

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[7] *J. Am. Chem. Soc.* **66**, 1362 (1944).

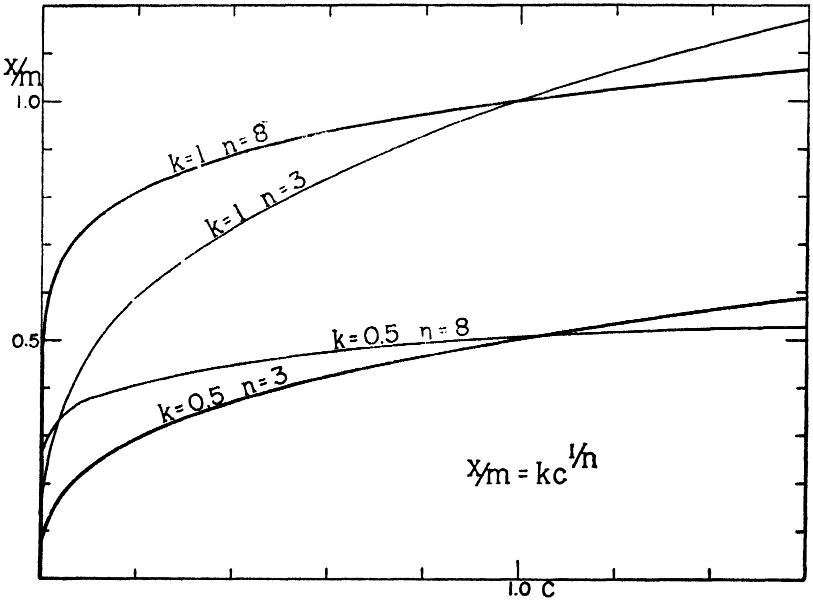

Fig. 4–8. Representative Freundlich isotherms.

$$\log x/m = -n \log P \text{ (or } -n \log c) \tag{4–11}$$

the Freundlich isotherm becomes a straight line. Isotherms can be conveniently plotted on log-log graph paper to yield a straight line. Figure 4–8 shows four Freundlich isotherms with various values of k and n.

Any comparison between the Freundlich and Langmuir isotherms must take cognizance of the different purposes for which the isotherms were developed. The Langmuir isotherm would only be expected to hold when adsorption is strictly monomolecular and there is only one type of surface. Sorption from solution sometimes obeys the Langmuir isotherm but more frequently there are deviations. The Freundlich isotherm is a purely empirical attempt to represent one type of curved line. It should be used only in the intermediate range since it is theoretically unsound at both ends.

At very low pressures adsorption is proportional to the pressure, or concentration. The Langmuir isotherm can be written

$$(x/m)/P = ab/(1 + aP)$$

and $(x/m)/P$ will equal ab when P is very small. The Freundlich isotherm gives

$$(x/m)/c = kc^{(1/n-1)}$$

and when c is very small $(x/m)/c$ becomes infinitely large because $1/n$ is less than one. This is contrary to theory and to experiment. At large pressures or concentrations sorption must reach a maximum yet the Freundlich isotherm predicts a continuously increasing sorption.

Both the Freundlich and the Langmuir equations apply to Type I isotherms and to the early part of Type II and Type IV isotherms. The B.E.T. isotherm applies to the entire range of isotherms of Types I, II and III and can be modified to include Types IV and V.

Other Methods of Representing Sorption.—The isotherm is not the only method of representing sorption data, although it is by far the most common. Any of the three variables, temperature, T, pressure, P, and amount sorbed, x/m, can be kept constant. If temperature is held constant we get an isotherm. Data at more than one temperature can be recorded on the same chart as a family of isotherms.

If we plot the quantity sorbed at constant pressure as a function of temperature we get an isobar (iso = equal, bar = weight or pressure). An isobar always falls as the temperature is raised for any one type of adsorption. This means that lowering the temperature increases adsorption. Nitrogen, for example, is only adsorbed in appreciable quantities at liquid air temperatures. The adsorption of all gases except helium is so strong on charcoal at liquid air temperatures that it can be used to obtain a very high vacuum. This method was used extensively before the advent of vapor diffusion pumps. Charcoal was contained in one part of the system and, when the system had been pumped down as far as possible by a mechanical pump, it was sealed off and the charcoal was surrounded by liquid air. The residual gases in the system were reduced by this treatment to a pressure of 0.05μ of mercury or less. This method is capable of reducing the pressure to 2 Å of mercury![8]

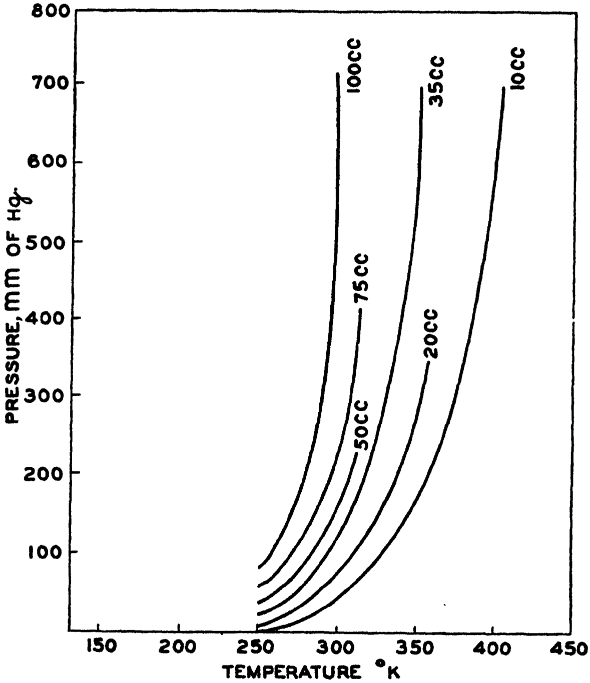

Fig. 4-9. Adsorption isosteres of ammonia on charcoal. (From Brunauer, *Adsorption of Gases and Vapors*, Vol. 1, Princeton University Press (1943).)

At very low temperatures all gases are adsorbed by van der Walls' forces and the adsorption will decrease with increasing temperature. As the temperature is increased further, a reactive gas may become adsorbed by chemical forces. The rate of attainment of chemical equilibrium is slow at low temperatures but increases rapidly with increasing temperature. In the region where chemical adsorption is slow it may be impractical to wait for equilibrium. It is customary to wait a standardized time, such as one hour or one day, and then measure the extent of adsorption. Such procedures will give a rising sorption isobar, but the exact position of the rising portion will depend upon the time allowed for equilibration.

If we hold the quantity sorbed constant and construct a graph of the pressure necessary to maintain a certain sorption as a function of temperature, we will get an isostere. Figure 4–9 shows isosteres for the sorption of ammonia on charcoal. An isostere is similar to the vapor pressure diagram of a solution and can be treated in the same way mathematically. Since adsorption falls off as the temperature increases at constant pressure, the pressure must be increased to maintain the same amount of adsorption. The slope of the isostere is related to the heat of adsorption and a plot of log P against $1/T$ will give straight lines whose slope is proportional to the heat of adsorption. Figure 4–10 shows the same isosteres of Figure 4–9 plotted in this way together with the calculated heats of adsorption. The heat of adsorption is greater than the heat of condensation for substances which obey Types I, II or IV isotherms.

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[8] Woodrow, J. W., *Phys. Rev.* (2) 4, 491 (1914).

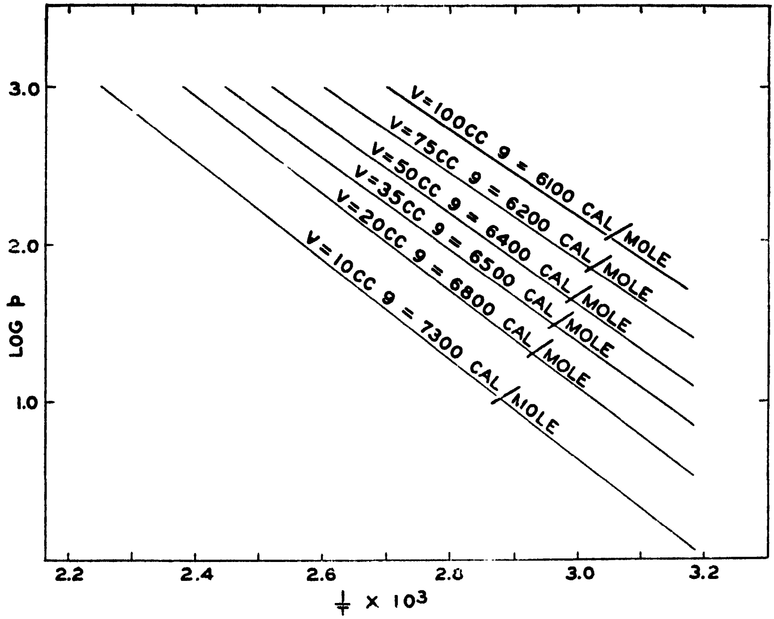

Fig. 4–10. The isosteric heats of adsorption of ammonia on charcoal. (From Brunauer, *Adsorption of Gases and Vapors*, Princeton University Press (1943).)

The heat of adsorption can also be measured directly in a calorimeter. This method as ordinarily applied gives an integral or average heat of adsorption which is less than the maximal heat of adsorption. The maximal heat of adsorption for Type I isotherms occurs at low values of x/m and may be several times the average calorimetric value.

The heat of sorption may be very large, particularly if chemical or even hydrogen bonds are formed. This is of practical importance when sorbents are used to remove large quantities of material. For example, the heat liberated by the adsorption of water on silica gel may raise its temperature 10° or 20° and reduce the adsorptive capacity.

✓**Practical Applications of Sorption.**—Sorbents are used industrially for recovery or purification of a large variety of substances. Gases and vapors, other than water vapor, are usually adsorbed on charcoal. Charcoal at room temperature is a universal adsorbent for all organic vapors but does not adsorb polar molecules such as water, Cl_2, HCN, HCl and NH_3 at low pressures. Organic vapors are strongly adsorbed at room temperatures but can be desorbed by steam. This useful property is employed in solvent recovery systems. Many industrial processes, such as the application of lacquers and the production of acetate rayon, involve large quantities of volatile solvents which must be removed by evaporation from the final product. Nearly all volatile organic solvents are inflammable and are a potential explosion hazard unless highly diluted with air. It is possible to pass the diluted vapors over charcoal and selectively adsorb all the vapors from a much larger volume of air. The adsorbed vapors can then be recovered by treatment with steam at 100° to 150° C. The vapors will come off with the steam and can be recovered by condensing the steam.[9]

Charcoal for adsorption purposes must first be "activated." Charcoal is prepared by heating wood or other organic material until the hydrogen and oxygen have been driven off as gases and vapors leaving a skeleton of carbon. The carbon in charcoal is frequently called amorphous carbon, but X-ray and electron diffraction examinations show that the carbon atoms are arranged in a graphite-like hexagonal structure, although the crystals may be only one layer thick. The porous structure of charcoal can be tremendously increased by controlled oxidation at elevated temperature. This procedure, which is called activation, increases the available surface area, either by opening up the pores so that they will let gas molecules penetrate, or by burning off adsorbed tars which cover the surface.

The purest charcoal can be obtained by heating sugar (sucrose), but charcoals from other sources may be more effective adsorbents. Bone char, which contains about 75% calcium phosphate, as a skeleton covered with carbon, is used to purify cane sugar syrups. Bone char is not so efficient per ton as some special charcoals, but it can be regenerated repeatedly at low cost. There is a large number of specialized charcoals, each adaopted to a particular process, such as decolorizing oils and aqueous solutions, removal of odors and noxious gases from air, and recovery of solvent vapors. Special alkali-activated charcoals are used to recover precious metals from very dilute solutions.[10]

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[9] See Luaces, E. L., *Alexander's Colloid Chemistry* 6, 840 (1946).

Activated carbon, U.S.P. (*United States Pharmacopoeia*) is an ingredient of the universal first aid antidote for poisons which have been swallowed. Charcoal is capable of adsorbing a wide variety of organic compounds—including strychnine, morphine, phenolphthalein, oxalic acid and phenol—and can be used even when the poison taken is not known. Charcoal has been frequently used as a treatment for stomach gas. The gases usually present are nitrogen, carbon dioxide and occasionally methane, none of which are appreciably adsorbed by wet charcoal at body temperatures. The charcoal does help, however; perhaps by adsorbing either the gas-forming bacteria themselves or some substance in the stomach which favors their growth.

Among other decolorizing agents, especially for oils, are the natural and activated clays. Fuller's earth, a clay-like mineral (see Chapter 11) has been used for centuries to remove grease from wool (one of the operations of fulling cloth). It is also used to remove undesirable impurities from petroleum, vegetable and animal oils. Fuller's earth removes color from lubricating oils and also removes substances which might produce gum; it is said to improve the lubricating qualities of the oil. Edible oils may be bleached and deodorized by Fuller's earth alone or in conjunction with charcoal. Acid activated bentonite clays are also used for much the same purpose as Fuller's earth. The action of these agents is very complex and, although there are many practical studies of the efficiency of various clays,[11] there are very few theoretical studies of the action of clays in nonaqueous systems. This should be a fruitful field for further research.

Silica gel, which is partially dehydrated polysilicic acid, SiO_2—xH_2O, adsorbs water, ammonia, and other polar molecules in preference to organic liquids. Silica gel (see Chapter 11) is made by treating sodium silicate with sulfuric acid. The orthosilicic acid, which forms first, polymerizes with loss of water to produce a finely porous gel structure containing water in the pores. The water content is reduced to between 4% and 7% by drying, leaving a hard glassy solid which is essentially porous silica. The remaining water is present as —OH groups on the pores and further drying causes collapse of the porous structure. Silica gel has a capacity for water vapor which varies nearly linearly with the relative humidity up to about 50% (Figure 4–11). A good grade of silica gel can hold 40% of its dry weight of water. When this gel is heated to about 150° C., most of the water will be driven off leaving about 5% as water of constitution. Silica gel can therefore be used to control humidity in air-conditioning plants. Some processes operate continuously, the granular silica gel being circulated through the air stream and then through an oven to revivify it. Silica gel is the most efficient desiccating agent for this purpose because of its high capacity.

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[10] Helbig, W. A., *Alexander's Colloid Chemistry* 6, 814 (1946).

[11] See Mantell, C. L.. *Adsorption*, Chapter 3 (1945).

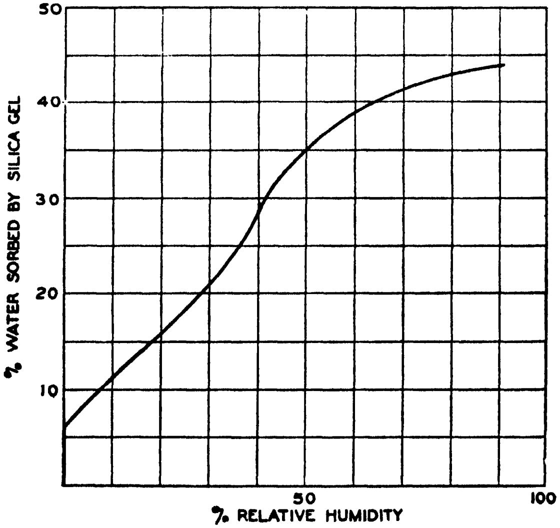

Fig. 4–11. Sorption of water by silica gel. (Redrawn from data supplied by F. C. Dehler of the Davison Chemical Corp., Baltimore 3, Md.)

The choice of a desiccating agent depends upon three independent factors: the desired final relative humidity or relative vapor pressure, the quantity of water which can be taken up, and the need for revivification. Silica gel is outstanding in the last two categories —it has a water holding capacity of 40% and it can easily be revivified; but it is not useful for drying air or organic liquids to "zero" moisture. Silica gel takes up water (above a minimum 5% water of constitution) almost linearly with increasing pressure but has very little capacity for water at very low relative humidities. Good drying agents, such as phosphorus pentoxide and magnesium perchlorate, may have a small total capacity but they will take up water vapor until they reduce the vapor pressure to extremely low values.

Activated alumina and some activated bauxites (florite) will lower the vapor pressure of water to 10^{-3} mm of mercury. Activated alumina holds water so strongly that it will not lose water even to phosphorus pentoxide. These adsorbents are in many ways much better desiccants than the conventional desiccants such as calcium chloride and sulfuric and phosphoric acids. All of these chemicals are corrosive liquids when saturated with water. Activated alumina and florite remain dry in appearance when saturated with water, are noncorrosive and can be regenerated by heating in an oven to 250° C. Heating drives off the water and the adsorbent is ready to be used again. Activated alumina has a useful capacity for water of 10% to 20% depending upon the final humidity desired. A special grade of activated alumina is prepared for dehydrating ethyl alcohol.

Large quantities of silica gel have been used to prevent corrosion of machinery in storage or while being shipped. The equipment is sealed up as tightly as possible and the silica gel adsorbs any moisture which may leak in. For this purpose silica gel, with its high capacity is the best desiccant. A desiccant which made the air drier (such as activated alumina) would not be any better from the standpoint of corrosion because corrosion is only serious at high relative humidities.

The determination of the water content of a colloidal material, such as flour, clay, or glass, is not a simple process. Drying to constant weight in an oven at 105° C. is a common procedure which works reasonably well on crystalline substances, such as sodium chloride, but is subject to many complications when applied to a colloidal system. The amount of water which remains in a stable colloidal system that is in an oven depends upon the temperature and the absolute pressure of water vapor in the air. The equilibrium conditions for a given vapor pressure of water are represented by the isostere for that pressure. The amount of water which is held by the colloid will be reduced as the temperature is increased, but there is no reason to expect all the water to be driven off at any practical temperature. One grade of silica gel, for example, retains 6% of moisture at 105° C. and will not lose all its water until it is heated to a temperature which destroys the material. Yet silica gel is a comparatively simple system that is not subject to many of the difficulties which are found in biological systems.

The rate of escape of water vapor from dense horny materials, such as dried proteins, is extremely slow and water vapor may continue to escape slowly for weeks or months. The limiting factor is the rate at which water molecules diffuse to the surface of the particles; this can be speeded up by reducing the size of the particles. Many biological colloids are unstable and they either decompose, liberating volatile substances such as ammonia, or they combine with the oxygen of the air and slowly gain weight. In either case the determination of the moisture from the loss of weight on drying is sure to be inaccurate. So difficult is the moisture determination that Gortner states: "*The determination of the moisture content of a biological material is a purely empirical procedure determined by the three variables, pressure, temperature, and time.*" [12]

The determination of the moisture by vacuum drying of the frozen material eliminates some of the difficulties caused by the chemical instability of the material. This technique, which is called lyophile drying, is described further on page 193.✓

Chromatographic Analysis.—Chromatographic analysis is a method for the differential sorption of a mixture of dissolved substances. It was invented by Tswett who used it to separate the pigments of green leaves. Although chromatographic analysis is not confined to colored substances (and for that reason is sometimes called adsorption analysis), it is much easier to work with those which are colored. The curious fact that Tswett's name means color in Russian could justify our use of the term chromatography even for colorless substances.

Tswett found that a mixture of pigments would be sorbed at the top of a column of a sorbent such as powdered magnesia. When the column is washed with additional solvent, the pigments are dissolved in the fresh solvent and re-adsorbed farther down. The pigment, which is least strongly sorbed, will be most easily washed off and will move fastest down the column. Pigments which are more strongly sorbed will not move as fast and some pigments may be sorbed so strongly that they cannot be washed off at all by that particular solvent. A polar solvent will be sorbed more strongly on a polar sorbent and will displace pigments more effectively than a non-polar solvent.

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[12] Gortner, R. A., *Outlines of Biochemistry*, p. 231 (1938).

Successful chromatographic analysis depends upon a very careful choice of solvent and sorbent. This choice can be aided by theory, but until recently the choice has been very largely the result of trial and error. The adsorption of any solute from solution is a balance between the affinities of each of the three components for the other two. When a dye is adsorbed on a surface of MgO from a benzene solution the attractive force of the MgO for the dye molecule is greater than the attraction of the MgO for the benzene. Furthermore, the attraction between the MgO and the dye is greater than that between the benzene and the dye. The amount of adsorbed dye varies both with the concentration of the dye and the quantity which is adsorbed. At low concentrations, some dye will come off the MgO and go into the benzene and at higher concentrations the MgO will adsorb the dye from the benzene. It may be difficult to predict the effect of a change in one of the components on the final equilibrium. If chlorobenzene were substituted for benzene, it might have a lower affinity for a non-polar dye favoring increased adsorption. It would also have a greater affinity for the MgO, and would compete with the dye for the surface. The result might be more easily determined by experiment than by theoretical reasoning.

Heterogeneous Catalysts.—A catalyst is defined as a substance which greatly increases the rate of a chemical reaction without being used up by the reaction. A heterogeneous catalyst is usually a solid which, when added to a gaseous or liquid system, speeds up the reaction. A common example, frequently quoted in elementary textbooks, is the catalytic oxidation of SO_2 to SO_3 on the surface of platinum. Catalytic processes are responsible for the greater part of the synthetic organic chemicals which have been introduced since 1930. High octane gasoline may be made by catalytic alkylation of low-grade petroleum products. The raw materials for most of the new plastics and synthetic rubber are made by catalytic methods. The conversion of liquid plant oils to solid cooking fats is brought about by hydrogenation, catalyzed by finely divided nickel; and there are few industrial organic processes today which do not use catalysis at some stage.[13]

Heterogeneous catalysis is always preceded by the adsorption of at least one of the reactive molecules on the surface. The forces of adsorption probably strain the adsorbed molecule so that it can react more easily with the other components; or, in some cases, the adsorbent may merely hold the adsorbed molecule in a favorable position for reaction. In any case, reaction takes place more readily on the catalytic surface than in the homogeneous fluid. It is necessary that the reaction product be desorbed readily if the catalyst is to have a large capacity.

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[13] See Emmett, P. H., *Alexander's Colloid Chemistry* 6, 214 (1946).

An adsorbed molecule may remain on a surface for as short a time as 10^{-10} seconds before reacting and releasing its place for another molecule. It is thus possible for a very small quantity of catalyst to tremendously increase the rate of a reaction. Any substance which is adsorbed on the catalyst, and is not desorbed again, will poison the catalyst. For example, traces of arsenic will poison the platinum catalyst used to oxidize SO_2 to SO_3 because the arsenic trioxide becomes permanently adsorbed on the surface of the platinum.

Most catalytic reactions involving gases take place at temperatures so high that physical or van der Waals' forces are ineffective. Adsorption of the reacting substances takes place almost entirely by chemical reaction with the surface. Langmuir[14] first pointed out that catalytic activity is a result of adsorption by chemical bonds. This is frequently called activated adsorption because of the large energy of activation.[15] Atoms at the surface of a crystal have unsatisfied valence bonds which can react with and adsorb gaseous molecules. Not all the molecules on a surface will have the same available energy for adsorption and only a small fraction of the surface may be catalytically active. Some catalytic reactions appear to take place only when the two ends of one of the reacting molecules are adsorbed by atoms far enough apart to strain the adsorbed molecules. For this reason it is frequently possible to poison a catalyst by the adsorption of a substance which covers only a small fraction of the total area. Sufficient carbon monoxide to cover 3% of the total area of a platinum catalyst will reduce the rate of hydrogenation of ethylene to one tenth of its initial value. The carbon monoxide is adsorbed preferentially on the active spots and the remaining area has very little catalytic activity. Taylor assumed that the active spots are atoms at the peaks or corners of the surface where they possess the maximum number of unsatisfied valence bonds.

Because catalysis by solids is primarily a surface phenomenon, catalysts are made with the largest available surface area. One convenient way to make a metallic catalyst is to precipitate it as a colloidal hydroxide on the surface of silica or some other colloidal solid. The metallic oxide can then be reduced to the free metal in a stream of hydrogen at high temperatures leaving a thin surface layer of metal on the porous carrier. The incorporation of other substances with the catalyst frequently has an enhancing effect on the catalytic activity. These accessory substances are known as promoters. Promoters may function by inhibiting the growth of crystals of the catalytic agent. The reduced metal is originally present as separate atoms on the surface of the carrier. If these atoms collect together to form crystals the effective area of the catalyst will be greatly reduced.

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[14] Langmuir, I., *J. Am. Chem. Soc.* **35**, 105 (1913), **38**, 1145 and 2221 (1916).

[15] Taylor, H. S., *Chem. Rev.* **9**, 1 (1931).

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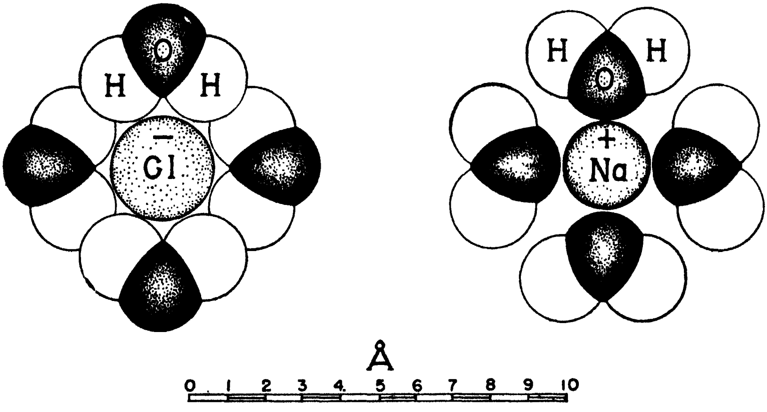
CHAPTER 5

IONIC ADSORPTION

Ions.—An ion is an atom, or a small group of atoms, which carries one or more elementary charges of electricity. The chloride ion, Cl^-, is a chlorine atom with one extra electron which gives it a single negative charge. A sodium ion, Na^+, is a sodium atom which has lost one electron leaving it with a single positive charge. The sulfate ion, $SO_4^=$, consists of five atoms and two extra electrons all bound together as the divalent sulfate radical.



A B

FIG. 5–1. A and B.

Ions have a strong electrostatic attraction for other ions of opposite charge and this attractive force holds together crystals of inorganic salts such as NaCl, K_2SO_4 and $(NH_4)_2$ HPO_4. Ions also have a strong attraction for dipoles, especially for the dipoles of small molecules which can approach close to the ion. When a salt is dissolved in water, the negative ions, such as the chloride ions, will be surrounded by as many water molecules as can crowd around them. The water molecules will be oriented with their hydrogen atoms toward a chloride ion. Figure 5–1a represents schematically the water molecules around a chloride ion. The positive ions, such as sodium ions, will also be surrounded by water molecules, but the positive charge will attract the negative end of the water dipole—that is, the oxygen atom. Figure 5–1b shows the arrangement of water molecules around a sodium ion.

Water molecules which are held to ions by ion-dipole interaction are not chemically bonded in the sense that the same water molecules stay with an ion all the time. There is rather a continuous interchange of water molecules, some leaving the ion and others taking their place. It is difficult to determine the exact number of water molecules which surround any given ion, but in general small ions have a higher potential and can hold a larger shell of water around them than large ions. Divalent ions will hold water more tightly than monovalent ions and many polyvalent ions hold one layer of water molecules by covalent bonds in a coordination shell (see Chapter 11). Table 5–1 shows one estimate of the size of hydrated alkali ions compared with the radius of the unhydrated ion obtained from X-ray studies of crystals.

Table 5–1

	Li^+	Na^+	K^+	NH_4^+	Rb^+	Cs^+
Crystal Radius in Å......	0.78	0.98	1.33	1.43	1.49	1.65
Hydrated Radius......... (approximate)	10.0	7.9	5.3	5.4	5.1	5.0

The attraction between ions and water molecules is so strong that water molecules will surround each ion and separate it from the ions of opposite charge. The attractive forces between ions is reduced as the ions are separated, and is further reduced if the medium between the ions has a high dielectric constant. Water has a much greater dielectric constant than any other common solvent, and water is therefore the best solvent for all ionic salts.

The individual ions in an aqueous solution have little or no tendency to associate together as ion pairs. For all practical purposes we can consider that the ions in a solution can move about independently of the ions of opposite charge, which are frequently called counter-ions. The only condition which must be satisfied is that a large number of ions of one sign cannot occur together in the absence of approximately the same number of counter-ions. Thus, although we can speak of the properties of chloride ions and can discuss the behavior of a single chloride ion, we can never get a bottle full of chloride ions. Whenever we have weighable quantities of chloride ions we must have an equivalent weight of sodium ions or some other cations.

The reason for this behavior lies in the charge on the ions. A single monovalent ion has a charge of 4.77×10^{-10} electrostatic units but, since there are 6×10^{23} ions in a mol, a liter flask containing one mol of chloride ions would have a potential of about 10^{16} volts! This is nearly a billion times the greatest potential yet produced by man.

The voltage produced by a collection of ions of the same charge depends upon their arrangement. When the charges are symmetrically distributed over the surface of a sphere (this is the most stable arrangement in a given volume), the potential, V, in volts is given by the equation:

$$V = 300\, en/Kr \tag{5-1}$$

where e is the charge on an election, 4.77×10^{-10} electrostatic units, n is the number of charges, K is the dielectric constant, and r is the radius of the sphere. A sphere with a volume of 1 liter has a radius of 6.2 cm; the dielectric constant of air is unity. The voltage is, therefore:

$$V = 300 \times 4.77 \times 10^{-10} \times 6 \times 10^{23}/6.2 = 1.4 \times 10^{16} \text{ volts.}$$

The charge on a colloidal particle 200 Å in diameter ($r = 10^{-6}$ cm) can be calculated in the same way. One hundred charges on this sphere would give it a potential of:

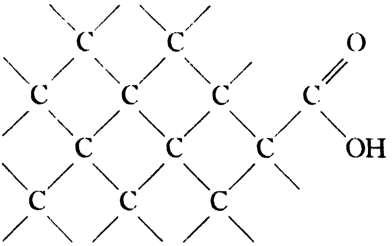
$$V = 300 \times 4.77 \times 10^{-10} \times 100/10^{-6} = 1.43 \text{ volts}$$

in air. If this sphere were in water, which has a dielectric constant of 80, the potential would be reduced to 0.18 volts, which is a large but not excessive voltage for a colloidal particle.

The area of a sphere 200 Å in diameter is $4\pi \times 10^4$ Å^2 and each of the 100 ions on the sphere would have an area of $4\pi \times 10^2$ Å^2. This is the area of a circle 20 Å in radius and the ions on the surface will therefore be about 40 Å apart. We might compare this separation with the separation of like charges in a 0.2 N solution of NaCl. In 10^3 cm^3 of solution there are 1.2×10^{23} Na$^+$ ions. Each ion has a volume of 8.3×10^{-21} cm^3 or 8300 Å^3. This is the volume of a cube about 44 Å on a side, so the separation of like charges in a 0.2 N solution is about the same as on a colloidal particle which has a potential of 0.18 volts. The solution, of course, has no net charge because it contains equal numbers of positive and negative ions.

✓ **Attached Ions and Ion Exchange.**—The word "ion" is derived from a Greek word meaning that which goes, and the term ion was originally applied to the particles which move in an electric field. We now think of ions as atoms or small groups of atoms which have one or more electric charges. It is quite possible to have an ion which is attached to a large particle or even to the wall of a vessel. Such an ion will not be able to go away from its point of attachment, but it will have all the other properties of an ion, including the requirement that there be a counter-ion (of opposite charge) in the near vicinity.

A particle of elementary carbon might, for example, have a carbon atom on its surface which was oxidized to —COOH.

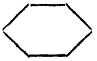


The oxygen and hydrogen atoms would be chemically adsorbed on the surface. In a basic solution this —COOH ion would ionize like any other organic acid to produce a —COO⁻ ion. Representing the un-ionized particle by RCOOH we can write an equation:

$$RCOOH + Na^+ + OH^- \longrightarrow RCOO^- + Na^+ + H_2O.$$

A collection of small carbon particles bearing —COOH groups can react as an acid by combining with NaOH to form a sodium salt and water. We can wash off all the excess hydroxide ions but it will not be possible to remove all the sodium ions by washing in water. The forces of electrostatic attraction will hold a number of sodium counter-ions equal to the number of $—COO^-$ ions on the particles. These Na^+ ions will not be held rigidly as an un-ionized salt —COONa, but the Na^+ ions will remain close to the $—COO^-$ ions.

We can remove the Na^+ ions from the particles only by a method which preserves the electroneutrality of the system. If we wash the particles with a solution of KCl, the potassium ions will replace the sodium ions. If we wash with enough KCl, all of the Na^+ ions will be removed and the particles will be left with K^+ instead of Na^+ as their counter-ions. The particles will have exchanged their Na^+ ions for K^+ ions and the process is known as ion exchange. Ion exchange may be defined as the process of replacing one counter-ion of an attached ion with a different counter-ion.

Substances which have appreciable ion exchange capacities must have large surfaces and are therefore colloidal. Only ions on the surface can exchange their counter-ions for other ions from the solution and a large surface is one criterion of a colloidal system. Substances which have a large ion exchange capacity are sometimes called zeolites, permutites, or base exchange materials (if the colloidal ions are negative with positive or basic counter-ions). The ion exchange capacity of a substance is usually expressed as milli-equivalents per hundred grams of dry colloid. The ion exchange capacity of soil colloids lies in the range between 10 and 150 ME/100*g*. Some synthetic ion exchange resins have capacities as great as 500 ME/100*g*. The structure of clay minerals will be dealt with in Chapter 11. Synthetic ion exchange resins consist of porous, cross-linked high polymers (see Chapters 6 and 7) which bear phenolate,  O^-; sulfonate, RSO_3^-; amine, RNH_3^+ or substituted amine, RR_3N^+ ions on their surfaces.

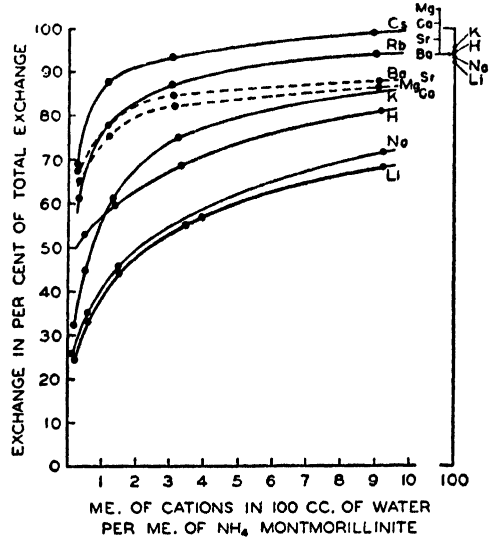


FIG. 5–2. Isotherms of various cations on an ammonia clay. (From Grim, *J. Geol.* **50,** No. 3, Fig. 8, p. 256 (1942). State Geological Survey, Urbana, Illinois.)

The exchange of one ion for another follows in many cases an adsorption isotherm. Figure 5–2 shows the behavior of a clay which had previously been saturated with ammonium ions, when treated with various quantities of electrolytes. Jenny[1] has developed a theory which satisfactorily predicts the adsorption isotherm in terms of what he calls the oscillation volume of the adsorbed ion in the neighborhood of the ion which is attached to the colloid. The oscillation volumes are proportional to the radius of hydration of the ions involved.

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[1] Jenny, H., *J. Physical Chem.* **40,** 501 (1936). See also, Vanselow, A. P., *Soil Sci.* **33,** 95 (1932); and Davis, L. E., *J. Physical Chem.* **49,** 473 (1945).

In general divalent ions will be held more strongly than monovalent ions by ion exchange adsorbants. Of the alkali ions, Li^+ is held the least strongly and Cs^+ the most strongly. This is in general accord with the radius of these ions in solution (Table 5–1). Lithium is a small ion in a crystalline salt but a relatively large ion in solution because it attracts a large number of water molecules. Potassium behaves as a much smaller ion than sodium in solution. The divalent ions, such as Ca^{++} and Mg^{++}, are still smaller. The smaller the radius of a counter-ion, the more strongly will it be held on the adsorbent.

Trivalent and tetravalent ions are usually adsorbed so strongly on ion exchange materials that they frequently cannot be removed by washing. In some cases the adsorption of a polyvalent ion may reverse the charge on the colloid. For example an Al^{+++} ion could combine with one monovalent anion on the surface as follows:

$$RO^- + Al^{+++} \longrightarrow R\text{—}O\text{—}Al^{++}.$$

The Al^{+++} can react with only one negative ion if these ions are far apart, and for each adsorbed Al^{+++} ion there will be two ⊕ charges on the colloid. Heavy metal ions are adsorbed strongly and frequently irreversibly by base exchange materials. The adsorption of precious metals by alkali activated charcoal may perhaps be accounted for by base exchange.[2]

The behavior of base exchange materials in acid solutions depends upon the strength of the acidic group which is bound to the colloid. Carboxylic acids, RCOOH, are weak acids and are ionized only in solutions more basic than pH 5. The clay minerals and related alumino silicates are also weak acids which are ionized only in neutral or basic solutions. When a base exchange material which contains ions of a weak acid is treated with a strong acid, the hydrogen ions are strongly adsorbed to form the un-ionized colloid. This adsorption is so strong in some cases that it resembles a homogeneous chemical reaction. Hydrogen ions are adsorbed more strongly than other cations because they form covalent links with basic anion whereas other cations are only held in the vicinity of the anion by electrostatic forces. The alumino-silicate colloids swell in acid solutions and become gelatinous and impermeable and are thus unsuited for use in acid media.

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[2] See Mantell, C. L., *Adsorption*, p. 144 (1945).

Modern synthetic ion exchange adsorbents have sulfonate, RSO_3^-, groups which are the ions of strong acids.[3] (Sulfonic acids are probably about as strong as the bisulfate ion HSO_4^-.) Hydrogen ions may exchange for sodium ions or other cations on these adsorbents in the same way that potassium ions exchange for sodium ions. A resin which is saturated with hydrogen ions will exchange its H^+ for any cation which is present in the solution that is brought in contact with it. If a solution of NaCl is passed through a column of an acid exchange resin, the solution which flows out will be HCl.

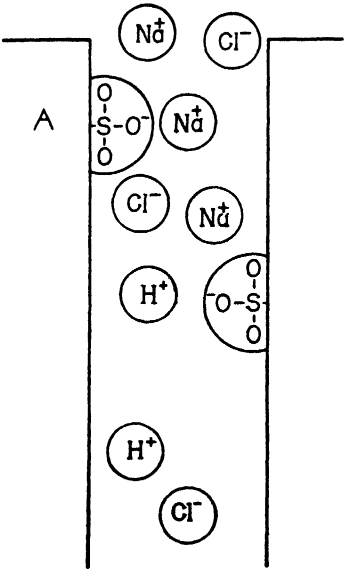

Fig. 5–3. Exchange of H^+ for Na^+ on an ion exchange column.

Even if there is no preferential adsorption of one ion in favor of another, the nature of ion exchange in a column is such that nearly complete replacement is to be expected. Figure 5–3 represents a column containing two negative ions and, originally, two hydrogen counter-ions. If the hydrogen and sodium ions were held equally strongly there would be an even chance that the first hydrogen ion at A would be replaced by the first sodium ion to pass it. The chance the hydrogen ion would not be replaced after n sodium ions had passed would be $(1/2)^n$. After only 10 sodium ions had passed the chance that the hydrogen ion would not be replaced would be $(1/2)^{10}$ or about 0.001. The exchangeable ions on a good adsorbent are spaced a few hundred Å apart which means that one millimeter of wall may contain more than 10,000 exchangeable ions. Even if the chance of replacement of one ion by another is less than one half we should expect replacement to be virtually complete in a very short distance along the column. Actual columns are not ideal in this respect because of the presence of channels between the granules, but relatively sharp fronts of displaced ions are found with properly packed columns.

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[3] Bauman, W. C., *Ind. and Eng. Chem.* **38**, 46 (1946).

As a solution of sodium chloride flows down a column containing exchangeable hydrogen ions, it will lose all its Na^+ ions and take on H^+ ions. The Cl^- ions will not be affected in any way. When all of the H^+ ions are replaced by Na^+ ions some Na^+ will appear in the effluent. The adsorption of ions on a column is of course one type of chromatographic adsorption, and it is sometimes possible to follow the progress of the adsorbed substance by a change in the color of the adsorbent.[4]

Anion, or acid exchange, resins consist of a porous solid material which contains amine or substituted amine groups. An amine will take up acids from solution as follows:

$$RNH_2 + H^+ \longrightarrow RNH_3^+.$$

A substance which has amine groups on its surface can be converted to an anion exchange adsorbent which has $\oplus$ groups on its surface by treatment with an acid. Some anion exchange substances have a positive charge in neutral solutions, but even very dilute alkalies will remove hydrogen ions and convert them to the un-ionized form. It should be possible to prepare anion exchange materials with quaternary ammonium ions. These ions form strong, highly dissociated bases and should produce a true hydroxyl ion exchange material.

Practical Applications of Ion Exchange.—One of the first applications of ion exchange was the use of natural zeolites to soften or remove calcium ions from hard water. Zeolites are naturally occurring porous silicate minerals containing Na^+ (or K^+) ions which are held electrostatically in the pores. A column of granular zeolyte will remove the Ca^{++} ions from hard water replacing them by Na^+. When the zeolyte is saturated with Ca^{++} it may be regenerated by washing with a strong solution of NaCl. Ca^{++} ions are held more strongly than Na^+ ions on the zeolyte and the regeneration is therefore aided by a higher concentration of Na^+ ions in the brine. The reaction is sometimes written:

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[4] Myers, R. J., Eastes, J. W., and Urquhart, D., *Ind. and Eng. Chem.* **33**, 1270 (1941).

$$CaZ + 2\ Na^+ \rightleftarrows Na_2Z + Ca^{++}.$$

Although this is not a simple homogeneous reaction, the laws of mass action hold qualitatively, and an increase in the concentration of the Na^+ ions will shift the equilibrium toward the right releasing Ca^{++} ions. Synthetic alumino-silicates having properties very similar to the natural zeolytes were introduced as permutites (by the Permutit Company among others) for water softening.

Synthetic resins containing replaceable cations can be used in a "sodium cycle" to remove calcium from water in the same way as the zeolytes are used. The synthetic ion exchange resins (and some others prepared by the sulfonation of carbonaceous products) may also be used in a "hydrogen cycle" to replace all of the cations by hydrogen ions. Salts in water can be quantitatively replaced by the corresponding acids; sodium sulfate, for example, being replaced by sulfuric acid. If the acid effluent from a hydrogen exchange column is passed through an anion exchange column, the acids will all be adsorbed and the resulting effluent will be ion-free or "demineralized" water. Demineralized water is nearly as pure as distilled water but may contain dissolved silica and CO_2. It is much cheaper than distilled water and, for many purposes, just as satisfactory.

It is necessary to keep the cation and anion exchange resins in separate containers *only* if you wish to regenerate the spent adsorbents. Nearly all of the reactive ions on the resins are present on the walls of pores in the granules where they are quite incapable of reacting with oppositely charged ions on other granules. A mixture of resin granules can be used to remove all ions from water, but the mixture cannot be regenerated once it becomes saturated with salts.

Ion exchange resins, particularly hydrogen ion exchange resins, have many uses in analytical chemistry. A mixture of iron and phosphates can be separated into two solutions, one containing all the phosphate as phosphoric acid, and the other solution, obtained by washing the column with HCl, which contains the iron as ferric chloride. It is not easy to determine either iron or phosphate in a mixture, but it is comparatively easy to carry out the determinations on the separate solutions.

The total quantity of cations in a solution can be determined by direct titration of the hydrogen ions in the effluent from a hydrogen ion exchange columns. Ion exchange columns can frequently be used to concentrate highly diluted polyvalent cations even in the presence of other salts, because polyvalent cations are selectively adsorbed on the exchange material. Not all ion exchange materials are suitable for analytical separations. Some may contain water-soluble substances which contaminate the effluent.

The purification and concentration of many organic chemicals can also be carried out on ion exchange resins. Excess acids can be removed from a solution by treating it with an acid exchange resin, without introducing any undesirable salts. Sugar occurs in plant juices as a solution which contain large quantities of ions. These ions inhibit the crystallization of the sucrose and are eventually concentrated in the molasses from which it is impractical to recover more sugar. Demineralizing of raw juices with ion exchange resins is a practical way of increasing the recovery of sugar from plant juice.

Soils consist of clay minerals, organic material called humus, and relatively inert granules of silica or other minerals. Both the clay minerals and the organic matter have ion exchange properties. The cation exchange capacity appears to be dominant, although there are references to anion exchange properties of soils. The typical base exchange properties of the clays resemble the zeolytes in some respects. The high exchange capacity of clays is due to a submicroscopic plate-like structure rather than to a porous structure such as is found in the zeolites (see Chapter 11). Potassium and ammonium ions are held more strongly than sodium ions and calcium ions are held even more strongly. Plants require four major elements from the soil, N, P, K, and Ca, and a number of minor elements. Nitrogen can be applied as ammonium salts or as nitrates. The ammonium salts will be adsorbed on the soil by a cation exchange reaction and will not be leached out as rapidly by irrigation. The same will be true for potassium salts. The anion exchange capacity of most soils is very low and nitrates are therefore not held in the soil but are readily removed by leaching. Calcium ions, applied as lime or gypsum, frequently replace potassium ions which were held at inaccessible points in the soil, and make them available for plant nutrition. By altering the pH of the soil, lime produces several other effects not directly related to ion exchange.

Although true anion exchange properties are difficult to demonstrate in soils, there are several specific mechanisms which produce adsorption of anions. A hydrogen clay will take up hydroxyl ions by direct reaction as follows:

$$RH + OH^- + Na^+ \longrightarrow R^-Na^+ + H_2O.$$

A clay which is saturated with calcium ions can also remove alkali in a similar way.

$$R^{=}\cdot Ca^{++} + 2\,OH^- + 2\,Na^{++} \longrightarrow R^{=}\,2\,Na^+ + Ca(OH)_2\downarrow.$$

Adsorbed calcium ions can also react with phosphate ions resulting in the sorption of the phosphate ions as precipitated calcium phosphate. The mechanisms discussed in this paragraph are not true anion exchange reactions because each is specific for only one ion. A true anion exchange mechanism would adsorb nitrate, chloride and sulfate as well as phosphate and hydroxyl ions, although some ions would be more strongly adsorbed than others. ✓

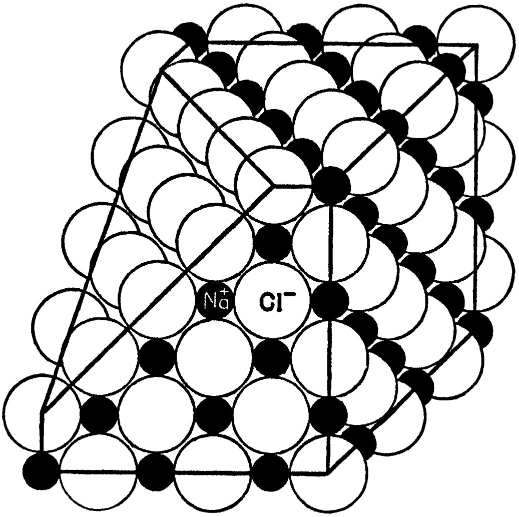

FIG. 5–4. Cubic and diagonal (or octahedral) faces of an NaCl crystal.

Adsorption on Ionic Crystals.—Crystals of common salts are composed of regular arrangements of ions which are held sogether by electrostatic forces. Each Na^+ ion inside a crystal of NaCl is surrounded by six Cl^- ions and each Cl^- ion is surrounded by six Na^+ ions. Figure 5–4 represents the arrangement of atoms on one face of a cubic crystal, such as NaCl. The normal cubic faces are shown and also a diagonal face. The cubic faces have equal numbers of positive and negative ions whereas the diagonal faces contain ions which are all of the same kind. A crystal grows because ions in the solution are attracted to spots on the crystal face where they fit exactly. An ion which is too large will not fit, and one which is too small will not be in contact with all its neighbors and will therefore be held less strongly than one which is a perfect fit. That is why crystals are usually pure even when they are grown in solutions containing several components.

The diagonal face of the crystal shown in Figure 5–4 is covered with Cl^- ions. This face will therefore have a strong electrostatic attraction for Na^+ ions. When covered with Na^+ ions it will adsorb Cl^- ions. The rate of adsorption of ions on the diagonal faces will probably be greater than the adsorption of ions on the square faces because of the greater electrostatic attractive forces, and the diagonal faces will therefore grow more rapidly. As a result of the greater rate of growth the diagonal faces will tend to disappear. It is easy to demonstrate on a diagram similar to Figure 5–4 that the preferential growth of any crystal face leads to the eventual disappearance of that face. The crystal faces which remain are therefore those which grow most slowly.

If sodium chloride is crystallized from solutions of urea, the crystals will have an octahedral shape. (An octahedron can be obtained by cutting off all eight corners of a cube.) Urea in some way inhibits the growth of the diagonal faces and the resultant crystals are therefore octahedra. The crystal faces are probably not perfect but consist of a mosaic of different layers of Na^+ and Cl^- ions resulting in a net zero charge on any face.

We do not know how urea is adsorbed on sodium chloride crystals, but other substances, including many dyes, have been studied by France.[5] He found that crystals of sulfates, such as potassium sulfate and alums, sorb dyes containing sulfonate groups on certain faces and that these faces grew more slowly and were therefore the dominant faces on the final crystal. The sulfonate group, RSO_3^-, on the dye has the same configuration as the sulfate ion, $OSO_3^=$, in the crystal, and it seems certain that the sulfonate ion of the dye fits into the place of a sulfate ion in the crystal. The rest of the dye molecule cannot fit into the crystal lattice and must therefore either create a flaw in the lattice or be desorbed before further growth takes place at that point. France found that only a very small fraction of the available places for sulfate ions on a K_2SO_4 crystal containing sorbed dye, were filled by dye ions. Most of the adsorbed dye ions are probably desorbed eventually, but not until they have inhibited the growth of the crystal face on which they were adsorbed.

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[5] France, W. C., *Alexander's Colloid Chemistry* 5, 443 (1944).

Foreign ions will be adsorbed on a crystal if they are strongly attracted to some spot on the crystal surface. This truism is the foundation of several rules for adsorption on crystals. The Paneth-Fajans rule states that those ions will be adsorbed which form a relatively insoluble salt with the ions of opposite charge in the crystal. For example, radium is strongly adsorbed on crystals of barium sulfate but not on silver chloride, because radium sulfate is very insoluble and radium chloride relatively soluble. In the same way one would expect iodide ions to be adsorbed on other silver halide crystals whereas fluoride ions would not be adsorbed.

The Paneth-Fajans rule is only qualitative in nature and there are various exceptions to it. It applies best to the adsorption of common ions of the crystal. Silver chloride crystals will adsorb Ag^+ ions from an excess of silver nitrate. These adsorbed cations will retain an equal number of anions, such as nitrate, as exchangeable anions. Conversely if silver is precipitated with an excess of chloride ions the silver chloride crystals will adsorb Cl^- ions. The adsorbed Cl^- ions will carry with them an equal number of exchangeable cations which cannot be removed by washing.

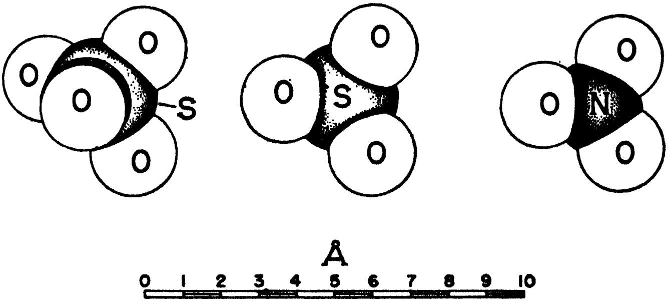
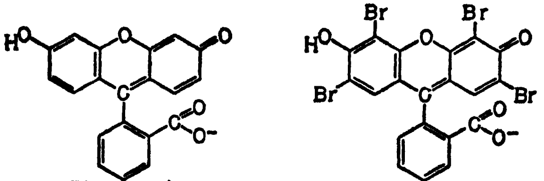


FIG. 5–5. Sulfate ions (two views) and a nitrate ion.

The number of adsorbed ions will never be sufficient to produce a monolayer of ions. A relatively small fraction of the available sites on the surface will be occupied by the adsorbed ions, and the electrical potential of these ions will repel others from the surface. The adsorption of ions on silver chloride is relatively unimportant from the point of view of gravimetric analysis, because the crystals are relatively large. Barium sulfate forms exceedingly minute crystals which have a large surface area and the adsorption of foreign ions is so serious that it is only possible to obtain quantitative results by techniques which balance the errors of adsorption. When sulfates are determined by precipitation with an excess of barium chloride, the Ba^{++} ions will be adsorbed and will carry along an equal number of anions. The precipitate will therefore contain an excess of barium chloride which produces high results. Nitrate ions have an aspect which resembles sulfate ions from one side (see Figure 5–5) and nitrate ions are adsorbed very strongly even in the presence of excess barium ions. It is probable that the surface of each barium sulfate crystal is covered with a layer of NO_3^- ions and sufficient Ba^{++} ions to make the surface essentially neutral.

Hydrogen and hydroxyl ions are strongly adsorbed on many surfaces, especially those of the metal hydroxides and the silicates (see Chapter 11). In acid solutions hydrogen ions will be adsorbed and will carry along an excess of exchangeable anions. Ferric hydroxide can be precipitated in the presence of acetic acid and the precipitate will carry down anions, such as sulfate, but not cations. If ferric hydroxide is precipitated from a basic solution, hydroxyl ions will be adsorbed and will carry down cations, such as magnesium, but not anions.

Some ionic dyes are adsorbed on ionic crystals only when there is an excess of precipitating ions of opposite charge on the crystals. Eosin is an organic dye anion which is adsorbed on silver iodide crystals when there is an excess of silver ions in solution. The silver salt of Eosin is insoluble but not as insoluble as silver iodide. Therefore when silver ions are added to a mixture of iodide ions and Eosin ions the silver iodide precipitates first. When all of the iodide has precipitated, silver ions will be adsorbed on the surface of the crystals and the Eosin ions will be adsorbed as a monolayer (probably incomplete) on the surface. The dissolved Eosin ions are yellowish but the adsorbed silver Eosinate is red. The change in the color of the system is very striking and Eosin is a good indicator for the titration of iodides. In order that the precipitate of AgI have as large a surface area as possible it is necessary to carry out the titration in very dilute



Fluorescein   Eosin

FIG. 5–6.

solutions. Dilute solutions inhibit the flocculation of small crystals and the production of curdy precipitates (see Chapter 12).

Eosin cannot be used as an indicator for the titration of chlorides with silver ions because the Eosin ion is strongly adsorbed on the precipitate, even in the presence of excess chloride ion. This proves that ionic attraction is not the only force which holds the Eosin ion on the surface of a crystal. Fluorescein is a suitable indicator for the titration of chlorides, although the color change is not so sharp as in the case of Eosin on iodides. Fluorescein has the structure shown in Figure 5–6a and Eosin is tetrabromo-fluorescein, Figure 5–6b. The bromine atoms in Eosin undoubtedly contribute to the attraction between the dye and a silver chloride crystal. In the presence of excess iodide ions, Eosin is not adsorbed because the iodide ions are adsorbed so much more strongly and they will replace the Eosin ions until all the iodide has been precipitated.

It is evident that the choice of an adsorption indicator depends upon a number of divergent factors, and it is difficult to predict in advance just which dye will work best in any particular system. Adsorption from solution is always a competitive affair and the presence of unrecognized impurities can interfere with the use of an indicator which is perfectly satisfactory in a pure system.

Dyes and Dyeing.—Water-soluble dyes are colored organic molecules which ionize in solution and are strongly sorbed by fabrics. Both cation and anion dyes are known and fabrics may contain bound anions or bound cations or may contain hardly any ions at all. The theories of dyeing are inevitably complex and are not made any easier by the nomenclature which grew up with the practice of dyeing before the theories were developed.[6]

Proteins are amphoteric substances which carry positive RNH_3^+ ions in acid solution and negative $RCOO^-$ ions in basic solution (see Chapter 9). They also contain large numbers of polar groups. Wool is a typical protein fiber, and it is not surprising to find that wool is dyed by anion dyes in acid solutions and by cation dyes in basic solutions. Anion dyes, such as Eosin, are frequently called acid dyes. They are ions of an organic acid and they have an opposite charge to the fabric in acid solution. Likewise cation dyes, such as Malachite Green, contain substituted ammonium ions, R_3NH^+, and are the ions of organic bases. They are frequently called basic dyes and are taken up most strongly from basic solutions.

The color of a dye is due to the absorption of light of certain wave lengths by the dye molecule. Those wave lengths will be absorbed which correspond in frequency to a natural vibration in the molecule. The frequencies of visible light are of the same order of magnitude as the frequency of electrons which are moving between resonating double bonds. Molecules which have several resonating double bonds will be colored and nearly all organic dyes consist of several aromatic rings linked by alternate single and double bonds. The group which confers color on a molecule is known as a chromophore.

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[6] See Valko, E. I., *Alexander's Colloid Chemistry* 6, 594 (1946).

The presence of mobile electrons greatly favors the formation of induced dipoles and accounts in part for the strong adsorption of colored substances on surfaces which contain many polar groups. Graphite consists of sheets of carbon atoms in a hexagonal structure with resonating electrons over the entire sheet. These loose electrons account for the electrical conductivity of graphite and for the black color, which means that it absorbs light of all visible wave lengths. Dyes are therefore strongly adsorbed on graphite and charcoal.

A good dye must contain some group which will bind it to a fabric. These groups are known as auxochromes, and may be either —OH, —NH_2 or —NR_2. The sulfonic acid group RSO_3^- is not an auxochrome. All natural fabrics contain groups which can form hydrogen bonds, such as $>\text{CMO}$ and $>\text{NH}$ in wool and silk, and —OH in cotton and linen. The function of the auxochrome group appears to be to form hydrogen bonds with the fabric and to hold the dye molecule firmly in place.

Wool contains sufficient polar groups capable of forming hydrogen bonds to attract most dyes quite strongly even when the wool and the dye ions bear charges of the same sign. Cotton (see Chapter 7) contains only a few anions and, although it is dyed by cation dyes, these dyes wash off easily. Trivalent and tetravalent metal ions, such as Al^{+++}; Fe^{+++}, Cr^{+++}, and Sn^{++++} and their hydroxides, are strongly adsorbed on cotton and their residual cation charges adsorb anion dyes. Metal salts which act as intermediate binders of dyes are called mordants. They have little use industrially because larger dye molecules have been prepared which will dye cotton directly. These are known as substantive dyes.

Substantive dyes, of which Congo Red is perhaps the most familiar example, are present in solution as colloidal aggregates. These aggregates are ionized and are colloidal electrolytes (see Chapter 9, page 214). The attractive forces between the organic part of the dye ions is sufficient to hold a number of ions together in a micelle, but electrostatic repulsion prevents the aggregate from growing so large that it will precipitate. Most dyes can be caused to aggregate by the addition of salts and some are rendered insoluble in saturated sodium chloride. This can be looked upon as an example of the common ion effect. In the case of Methylene Blue chloride the reaction may be written:

$$\mathrm{MeB^+ + Cl^- \longrightarrow MeBCl \downarrow .}$$

Addition of chloride ions forces the reaction to the right and the dye precipitates.

Substantive dyes may be precipitated in the pores of the cotton. Cellulose may also favor the aggregation of the molecules to form particles too large to diffuse out again. It is common practice to reduce the solubility of a dye and fix it on the cloth by the addition of salts to the dye bath when the dyeing is nearly completed. Some dyes are present in a soluble form in the dye bath and are converted to insoluble forms after they have diffused into the fibers. Indigo is reduced to a soluble colorless leuco base in the dye bath. This reduced form can enter the pores of the fibers. The insoluble color is developed when the fabric is dried and exposed to the oxygen of the air. Ice colors are diazo-dyes which are made after the component molecules have diffused into the fibers. The resultant dye molecule is too large to diffuse out again. The diazotization is carried out with nitrous acid in ice cold solutions; hence the name "ice colors."

The adsorption of dyes by fabrics follows a typical isotherm which can be represented by the Freundlich equation (4–9). The sharpness of the corner of the isotherm, which is proportional to the value of n in the Freundlich equation, is a good measure of the fastness of the dye to washing. A fast dye is one that is strongly held on the fabric in very dilute solutions. Very fast dyes are desirable from the consumer's point of view but may be impractical to apply. A dye which is sorbed too tightly will become fixed to the first portion of the fabric to enter the dye bath, coloring it too deeply, and there will be insufficient dye to color the remainder of the material. It is necessary to use a dye which is held sufficiently loosely to the fabric in the bath so that the dye molecules can migrate from regions where the dye is too dark to those where it is too light. Adsorption is reduced by increasing the temperature and it is therefore customary to apply dyes from boiling solutions where the dye is less strongly adsorbed.

Histological Stains.—Histological stains frequently consist of simple dyes which are molecularly dispersed in solution. Colloidal dyes would not be able to penetrate through the protein membranes of the tissue and reach the inside of the cells. The large differences in the uptake of different stains by different structures in the cell is the basis of differential staining. Cell nuclei contain nucleo-proteins which are complex substances containing substituted phosphate anions. Most of the cytoplasmic proteins carry more cations than anions. Nucleo-proteins stain very strongly with basic, cationic dyes and there is some evidence that the dye forms an undissociated salt linkage with the phosphate radicals of the nucleic acid.[7] Cytoplasm takes up acidic anionic dyes. Salt type linkages between ions of opposite sign are not the only determining factors in histological staining. Other parts of the dye molecules are undoubtedly attracted to the tissue just as in the case of the dyeing of fabrics. Some tissue structures have a fatty nature and can only take up those dyes which are non-ionic. This may be a case of true solution and *ab*sorption of the stain.

The complicated nature of tissue staining is inevitable in view of the wide variety of tissue materials, and the stain technologists desire to produce a specific stain for each of the structures present in the cells. The uptake of the stains by the cellular material is certainly covered by the all inclusive term, sorption. The uptake of a molecule by chemical reaction with a specific point on the surface of a colloidal particle is better described as chemical adsorption, rather than as chemical reaction, since not all of the active points will be equally accessible to the reagent.[8] The term sorption includes not only surface reactions but also solution and adsorption and is therefore the term which best covers the field.

The sorption of ions by solid materials is rendered exceedingly complex by the variety of types of sorption which are possible. You should therefore not expect to understand all of the published results in terms of the few generalizations which have been set down in this and the preceding chapters. The general principles certainly apply but it may be difficult to pick out the one which is primarily responsible for the observed effects.

Before going on to the next chapter it may be well to collect together the different mechanisms which influence the attachment of a dye to a solid:

1. The dye may be dissolved in or *ab*sorbed by the solid, in which case the laws of solubility (see page 118 ff.) will govern

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[7] See Stearn, A. E., and Stearn, E. W., *Stain Technology* 4, 111 (1929); 5, 17 (1930).

[8] See Holmes, W. C., *Stain Tech.* 4, 75 (1929); and Conn, H. J., *Biological Stains*, 4th Ed., p. 188 (1940).

the relative concentration of the dye in the solid and in the surrounding solution.

2. The dye may be adsorbed on the surface by van der Waals' forces where it will compete with other adsorbed substances including the solvent. Hydrogen bonds are the most important of the van der Waals' forces which hold ions to a fabric or tissue. Items 1 and 2 are common to ions and molecules, although ions are usually only slightly soluble in nonaqueous systems.

3. The dye may be held by ion exchange as a counter-ion near an ion of opposite charge on the surface. The presence of an excess of electrolytes in most dye solutions usually eliminates this possibility.

4. The dye may form an un-ionized salt linkage with ions of opposite charge. This item differs only in degree from the previous one as it is impossible in many cases to make a practical distinction between an ion pair and an un-ionized molecule.

5. A combination of 2, van der Waals' attractions, and 3 or 4, electrostatic linkages, undoubtedly account for a large number of common reactions between dyes and tissues or fabrics.

6. The dye may react chemically with the solid to form a covalent link. This is not common with ordinary staining techniques but dyes have been coupled by diazo links to the aromatic rings which are present in most proteins.

7. The dye may be physically trapped by crystallizing inside a pore from which it cannot escape.

8. Any combination of the preceding possibilities may occur.

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CHAPTER 6

HIGH POLYMERS

Polymerization.—High polymers are substances whose individual molecules are of colloidal dimensions. Ordinary noncolloidal molecules have molecular weights less than 1000 and more frequently are of the order of 100. In contrast, the substances classed as high polymers have molecular weights ranging from about 10,000 up to several million. Since each molecule is in itself a colloidal particle, the high polymers represent one of the simplest types of colloids, yet their properties have only recently been explained in terms of their structure. The natural high polymers include all the common organic structural materials such as wood and cotton; silk, horn, hair, and wool; the proteins of meat and eggs; starch and rubber. The synthetic high polymers include the now familiar plastics, synthetic fibers such as nylon and synthetic rubber. Although the earliest organic chemists prepared synthetic high polymers, they discarded them, as did most of their successors, as "unresolvable tars" since they cannot be distilled or crystallized from solution and have no sharp melting points. Derivatives of natural high polymers came into use in the form of celluloid and gun cotton about 1870. Bakelite, the first successful synthetic high polymer, was produced by Leo Baekeland in 1908.

We may define a molecule, for the purpose of this work, as a collection of atoms bound together by covalent bonds. Table 6–1 lists the energies necessary to break various types of covalent bonds. The values given represent the energy in kilocalories necessary to rupture 1 mol of a substance at the indicated bond. To determine the strength per bond it is only necessary to divide by Avogadro's number. To this list of molecular bonds might be added some unionized salt linkages in organic compounds. Salts which ionize in solution are, of course, present as ions, not molecules. We will not consider as molecules those crystals which are held together by electrostatic forces such as the ions in a crystal of sodium chloride or the ions and free electrons in a metal. Table 6–1 also lists some tentative values for the energy of molecular cohesion.

Many high polymers can be produced by the combination of one or more types of small molecules; these are called monomers. The

TABLE 6–1. BOND ENERGIES IN KILOCALORIES PER MOL*

Covalent Bonds	
$-C\equiv C-$	123
$>C=C<$	100
$>C-C<$	59
$>C-O-$	70
$>C-N<$	59
$>C-S-$	54
$-S-S-$	64
$>Si-Si<$	42
$>Si-O-$	90
Ionic Bonds	
Na^+, Cl^- (dry)	128
$-NH_3^+$, $-COO^-$ in water	4.5

Intermolecular Cohesion	
$>C=O \cdot\cdot H-N<$	10–16
$>C=O \cdot\cdot H-O-$	7–10
$>COH \cdot\cdot HOC<$	14
$H_2O \cdot\cdot H-O-H$	5
$-NO_2{:}O_2N-$	7
$-COOR{:}ROOC-$	6
$-HC=O{:}O=CH-$	5
$-Cl{:}Cl-$	3
$-CH_3{:}H_3C-$	2
$O_2{:}O_2$	2
$-O-{:}-O-$	1.6
$-CH_2-{:}-CH_2-$	1.0
$H_2{:}H_2$	0.25

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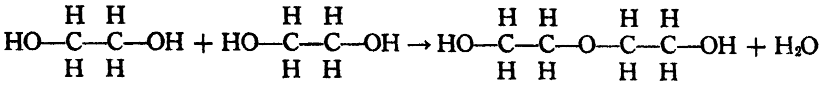
* Convalent bond energies according to Pauling, *The Nature of the Chemical Bond.* Intermolecular cohesions from Dunkel and Wolf according to Mark, *High Polymers* **2,** 112 (1940).

simplest type of high polymer is made by the repeated addition of the same monomer unit to a parent molecule. For example, ethylene glycol could add to itself by loss of water to make the ether, called di-ethylene glycol.



$$HO-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH + HO-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH \rightarrow HO-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-O-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH + H_2O$$

To this molecule can be added additional ethylene glycol molecules in the same way and, since it will always have a hydroxy group at each end, it is always possible for the molecule to grow larger. The practical upper limit of size depends on the purity of the starting material since impurities such as ethyl alcohol could add to the chain but would stop further growth in that direction unless removed. Figure 6–1 represents part of a chain of polyethylene glycol. Industrial preparations of polyethylene glycol have been made with molecular weights as great as 120,000, corresponding to 8000 atoms in line. Carbowax is one trade name for this high polymer.

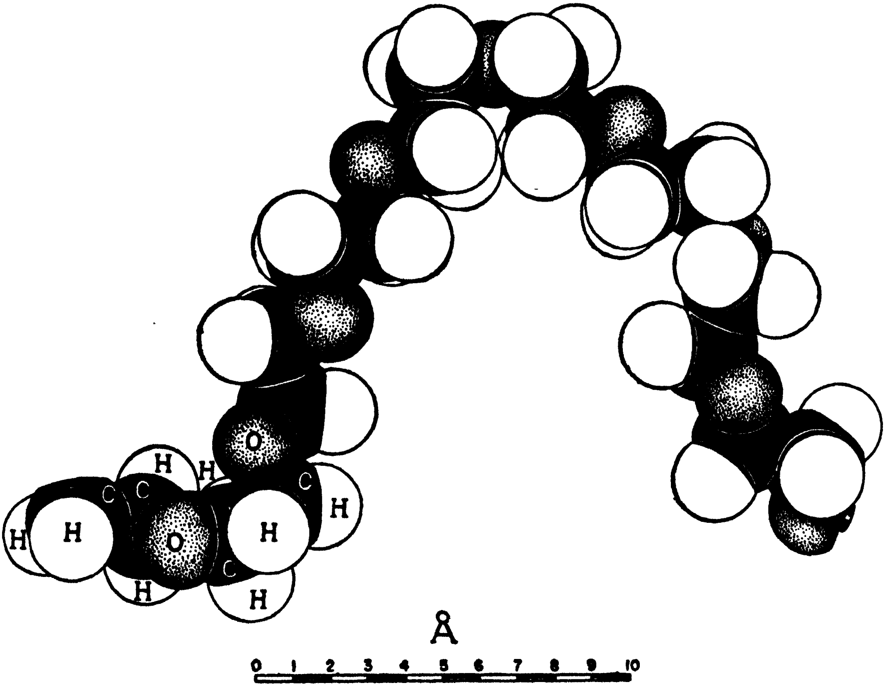


Fig. 6–1. Polyethylene glycol.

High polymers can be made by the reaction of any substance, or group of substances, whose molecules contain two or more groups capable of linking with one another. Hydroxy acids may react to form long chain esters, and very similar products can also be made from equimolecular mixtures of dicarboxylic acids and glycols. Likewise amino acids condense to form the polyamides of proteins and dicarboxylic acids react with diamines to form polyamides such as Nylon. Aromatic molecules such as phenol can be linked with formaldehyde to form polymers (see Chapter 7.) These products were formerly known as Bakelite before that term became a trademark designating plastics produced by a certain company. Amines such as urea and melamine are also linked with formaldehyde to produce useful plastics.

Another type of polymerization involves the reaction of unsaturated molecules to produce a polymer having the same empirical formula as the monomer but less unsaturation. For example, ethylene condenses with itself to produce essentially saturated paraffinic hydrocarbons of very great molecular weight. The mechanism involves free radicals and will be discussed in Chapter 7.

The atoms of polyvalent nonmetals are potentially able to join with themselves to make high molecular weight polymers. The most familiar example of this type is rubbery sulfur formed by the opening of the S_8 rings of monoclinic sulfur and the polymerization of these short chains of eight sulfur atoms to form very long chains.

Diamond, which is pure carbon, also represents a high polymer since the carbon atoms are bonded together by strictly covalent bonds which extend in all directions throughout the crystal. Graphite consists of flat layers of carbon atoms arranged in a continuous aromatic ring structure. The layers are bonded together by much weaker cohesive forces. This structure accounts for the soft, slippery properties of graphite since the cohesive forces between the layers are weak enough to permit them to slip over one another. Silicates can be considered to be polyanhydrides of ortho-silicic acid containing long chains of $—\overset{|}{\underset{|}{\mathrm{Si}}}—\mathrm{O}—\overset{|}{\underset{|}{\mathrm{Si}}}—\mathrm{O}—\overset{|}{\underset{|}{\mathrm{Si}}}—\mathrm{O}—\overset{|}{\underset{|}{\mathrm{Si}}}—\mathrm{O}—$ which may be further joined by oxygen cross links to give silica or may contain metallic oxide substituents as in the silicate minerals. Many other minerals and insoluble compounds are linked together by continuous covalent bonds and can be considered to be high polymers.

Properties of High Polymers.—The primary property which distinguishes high polymers from other molecules is, of course, molecular weight. For polymers formed from difunctional monomers the chain length is proportional to the molecular weight, and many physical properties are correlated with the chain length. It is convenient to define chain length as the number of atoms in line in the longest chain through the polymer. This is not quite the same as the degree of polymerization, DP, which is the number of monomeric units in a chain. Obviously a chain consisting of 100 units of a monomer which has only 2 atoms will be only one fifth as long as a chain containing 100 units of a monomer which has 10 atoms in line.

Synthetic high polymers always consist of a mixture of molecules of different sizes. Since the growth of any one chain is essentially a random process some chains will become longer than others. The product will not have a single molecular weight but there will be a distribution of molecular weights such as is shown in Figure 6–2. The mechanical properties of a mixture are not the same as those of a pure substance with the same average molecular weight. Separation of pure samples of identical molecular weights is not prac-

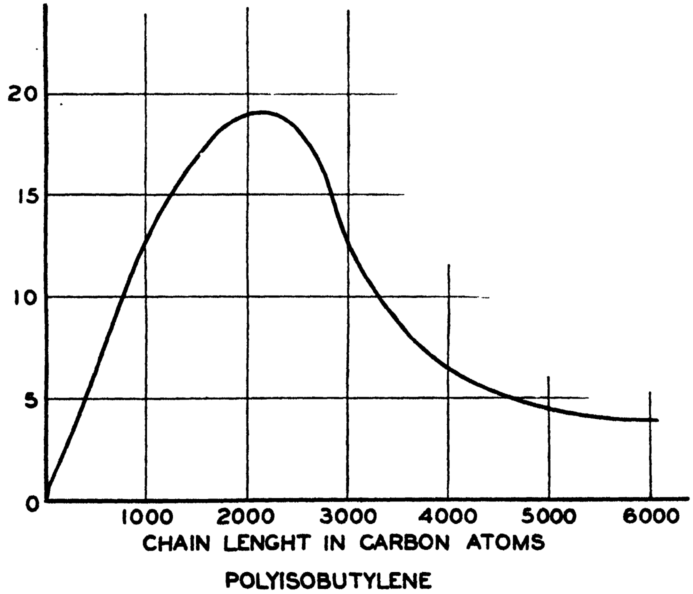


Fig. 6–2. Experimental distribution curve for polyisobutylene. P is the number of monomers in the polymer. (Redrawn from Mark in *Science in Progress*, 3rd series, Yale Univ. Press (1942).)

ticable for most high polymers because the properties of the different molecules are so nearly identical. By careful fractional precipitation from solution it is possible to prepare mixtures having a small range of molecular weights, but often the properties of the original mixture are superior to the properties of any of its fractions. Fractionation is, however, the only available method for determining the composition of mixtures of high polymers.

Since most high polymers consist of mixtures, an average molecular weight may be used for descriptive purposes. There are at least two average molecular weights in use. The "number average" is the total weight divided by the total number of molecules. It can be obtained directly from osmotic pressure measurements in sufficiently dilute solutions or by any other method which counts molecules. The "weight average" is obtained by multiplying the weight of each molecular species by its molecular weight and dividing by the total weight. Small molecules have much less influence on the weight average, which is also more closely correlated with the viscosity in solution and other physical properties of the substance than is the number average molecular weight.

Mechanical strength in polymers is found only in molecules which have a chain length greater than about 150 to 200 atoms in line. Shorter chains produce oils or brittle crystals such as paraffin. As the chain length is increased up to about 500, there is a rapid increase in strength, but beyond that point the strength increases more gradually with increasing length. Molecules which have strong attraction for each other will of course produce stronger substances at low molecular weights than molecules which attract each other only weakly.

Since even very long chains of several thousand atoms extend less than one micron, the strength of a high polymer lies in the attractive forces between chains. These attractive forces are the same forces which produce physical sorption and which hold molecular crystals together. Per atom these forces are not great but if there is sufficient overlap between chains the attractive forces will add up and the substance will have strength. Cohesive forces between chains vary from 1 kilocalorie per mol for 5 Å of hydrocarbon chain up to nearly 10 kilocalories for 5 Å of silk fibroin. Mechanical entanglement of the type found in felt also contributes to the strength of a polymer composed of long chains. It is even more evident in solutions where it contributes to the high viscosity of relatively dilute solutions of high polymers like rubber in benzene or starch in water.

The longer the chain the more viscous the solution at the same weight concentration.

When a polymer composed of essentially linear chains is heated, it will soften over a relatively narrow range of temperature to give a viscous or plastic fluid. In this state it can be forced into molds by the application of high pressure and will retain the shape of the mold after cooling.

The melting temperature is greatly reduced by bumps or other irregularities on the chain since these keep the chains from fitting closely together. The attractive forces which hold the molecules together as a solid are short-range forces and are effective only at the points where atoms touch each other. Any factor which prevents the close approach of two chains will reduce the attractive forces and as a result thermal energies will exceed cohesive energies at a lower temperature. In other words, the compound will have a lower melting point. A few linear polymers, such as starch and cellulose, do not melt because they decompose at temperatures below their melting point.

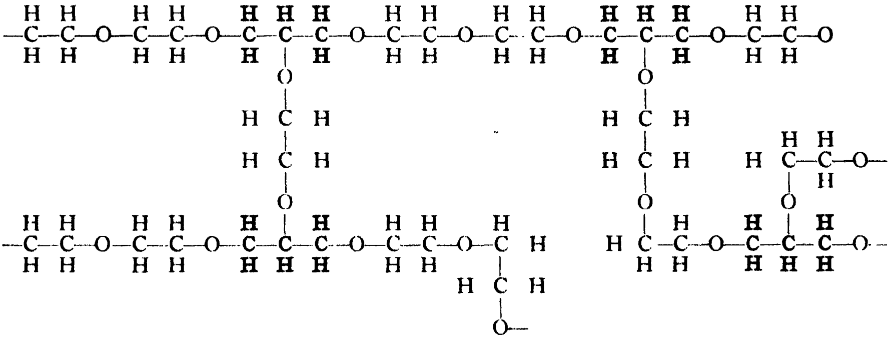


FIG. 6–3. A diagrammatic representation of part of a copolymer of ethylene glycol and glycerine. Glycerine molecules are shown in bold face type.

Not all polymers are composed of linear chains. If some of the monomers are capable of reacting with more than two other molecules it is possible to obtain polymers with branched chains and also chains which are tied together in a net by cross linkages. If ethylene glycol were polymerized with glycerine (trihydroxy propane), each glycerine molecule would give rise to a branch, so that a portion of the final polymer might resemble Figure 6–3.

At low degrees of polymerization the presence of tri- or tetrafunctional monomers will produce branched chains which usually do not cause very great changes in the physical properties of the polymer. At a certain point in the reaction, the branched chains will begin to tie together and a relatively small amount of further reaction will tie all the molecules together by covalent bonds. When this stage is reached the material becomes solid and will neither melt nor dissolve. Both melting and solution involve movement of the molecules of the substance relative to each other and, if all the material is present as one molecule, it obviously cannot become fluid. A cross-linked polymer can contain a large proportion of small molecules and still have rigidity, although a product with relatively few cross linkages and containing a large proportion of liquid molecules will have the properties of a gel.

Solvents and Solubility.—Before discussing the behavior of high polymers in solution it is desirable to discuss a few facts about solubility in general. The one general statement that can be made regarding solubility is that similar substances are soluble in each other. This means that hydrocarbons will be soluble in hydrocarbon solvents and esters will be soluble in ester solvents. A portion of a long hydrocarbon chain has about the same aspect as a molecule of a short hydrocarbon solvent, and the interatomic attractions will also

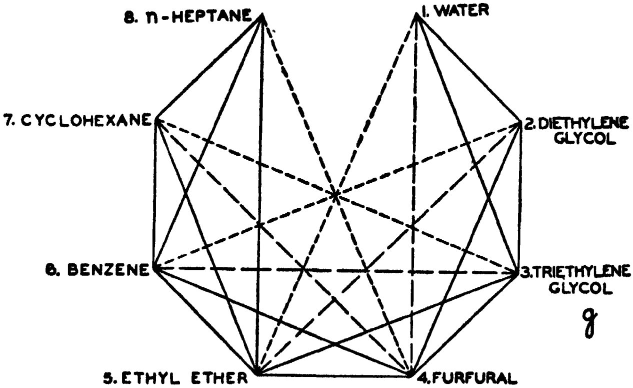


Fig. 6–4.

———————— Complete miscibility; — — — — — — — — High solubility; - - - - - - - - - - - - - - - - - Low solubility; No line—Very low solubility.

1. Water. 2. Diethylene glycol. 3. Triethylene glycol. (3.7. Methyl alcohol. 4. Furfural. (4.3. Ethyl Alcohol.) (4.6. Acetone.) 5. Ethyl ether. 6. Benzene. 7. Cyclohexane. 8. n Heptane.

(From A. W. Francis, *Ind. and Eng. Chem.* 36 (1944), with permission of the American Chemical Society.)

be of the same order. Therefore high polymeric hydrocarbons should also be soluble in hydrocarbon solvents.

On the other hand, although hydrocarbons have some attraction for solvents like water, the water molecules are attracted so much more strongly to other water molecules that hydrocarbon molecules are squeezed out and we find that hydrocarbons are not soluble in water. Francis[1] has arranged some common solvents in a series from water to *n* heptane (Figure 6–4). In this figure heavy lines indicate high solubility and dashed lines indicate lesser solubility.

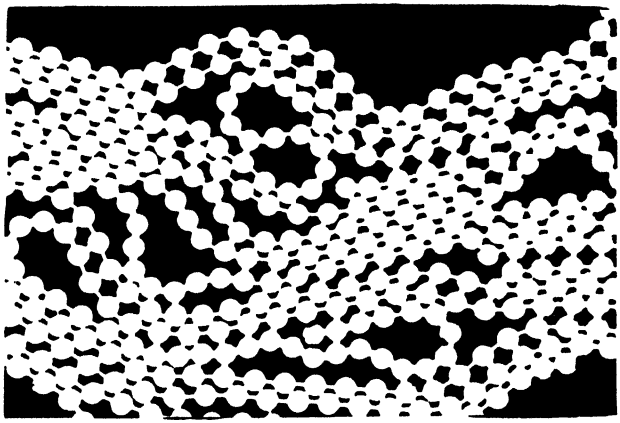


FIG. 6–5. A schematic representation of micro-crystalline regions of a high polymer.

The series presented in Figure 6–4 reflects the intermolecular forces existing in solvents. These forces have sometimes been interpreted as producing an internal pressure in the liquid. The internal pressure may be defined as the effective force per unit area which holds the molecules of a liquid together against the dispersive forces of thermal agitation. Water has a high internal pressure and heptane has a low internal pressure. The other solvents have internal pressures intermediate between these two extremes. Unfortunately there is no direct way of measuring the internal pressure and there is only qualitative agreement between various estimates of the internal pressure of common liquids. The series presented in Figure 6–4 is as useful as any other tabulation of internal pressures.[2]

Since intermolecular forces depend on contact between atoms, molecules which fit well together will have many points of contact and will form stable crystals. Solvent molecules will usually be unstable to penetrate the crystal lattice but some molecules from the crystal will escape and dissolve in the solvent. Many high polymer chains fit together like a bundle of sticks, forming a kind of crystal structure. This crystalline structure is ordinarily not perfect, and a single long chain may pass through several crystalline regions and intervening amorphous regions. Figure 6–5 shows this behavior schematically. Solvents will probably be able to enter the amorphous regions of such a micro-crystalline high polymer and cause swelling but they will not be able to penetrate the crystal lattice. A substance having this structure will swell but not dissolve much below its melting point. Polyethylene appears to be such a polymer. Below about 80° C. it is insoluble in all solvents, although it may be swollen by hydrocarbons and chlorinated solvents. The interatomic forces in polyethylene are not large, but the chains are so regular that parallel chains will fit closely together with a maximum number of points of contact.

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[1] Francis, A. W., *Ind. and Eng. Chem.* 36, 1096 (1944).

[2] See Glasstone, *A Textbook of Physical Chemistry*, 2nd Ed., p. 479 (1946).

In addition to general similarities between solvent and solute, certain specific attractive forces must be considered. The hydrogen bond is by far the most important of these forces in common systems. Hydrogen bonds are formed by hydrogen atoms of $—OH$, $=NH$ (and to a lesser extent $—CCl_2H$) which are strongly attracted to other oxygen, nitrogen, or fluorine atoms. Water molecules can both give and receive hydrogen bonds with an energy of 4 to 5 kilocalories per mol. Hydrogen bonds between alcohols and organic acids have energies between 6 and 8 kilocalories per mol. The hydrogen bond is too weak to be ranked with other covalent bonds but stronger than other van der Waals' attractive forces (see Table 6–1).

Water, because of its ability to form hydrogen bonds, is a good solvent for substances having many groups which can form hydrogen bonds. Examples of these groups in order of decreasing affinity for water are $—COOH$, $—CONH_2$, $—OH$, $—NH_2$, $=NH$, $\equiv N$ and $R—O—R$. Compounds soluble in water may also be soluble in lower alcohols. Conversely heptane, gasoline, benzene and chlorinated hydrocarbons are good solvents for polymers consisting primarily of hydrocarbons. Ketones and esters are good solvents for polymeric esters, and chloroform is a surprisingly good solvent for this class because the three chlorine atoms activate the hydrogen enough to permit hydrogen bond formation. Carbon tetrachloride, on the other hand, is a solvent of the hydrocarbon type.

Mixtures of solvents are frequently much more effective than any single solvent. There are various explanations for this phenomenon. The most plausible theory takes account of the fact that the solute may have different groups which are specifically attracted to different solvents. For example, Palit[3] found that sodium oleate, $C_{17}H_{34}COONa$, is insoluble in either chloroform or ethylene glycol but is soluble in a mixture of the two. Chloroform is a solvent for the long carbon chain and glycols are good ionizing solvents for the carboxyl group and the sodium ion. Together they are able to dissolve the soap.

There are other cases in which this explanation does not appear to hold. For example, rubber, an unsaturated hydrocarbon, is soluble in a mixture of hexane and acetone but not in either solvent alone. It is also soluble in pure benzene. From the tabulation in Figure 6–4, it is apparent that a mixture of acetone and hexane might have an internal pressure close enough to the internal pressure of benzene to make it also a solvent for rubber.

Swelling and Gelation.—When a high polymer is treated with a small quantity of a good solvent the solvent molecules will penetrate between the polymer chains and cause the polymer to swell. If the chains are all lying in the same direction in a fiber, the cross section of the fiber will swell but the length will remain unchanged. Films formed by the removal of solvent from a layer of polymer solution swell in thickness much more than in either long dimension.

As more solvent is added to a linear polymer the structure will continue to swell, and individual molecules will slowly go off into solution. If the polymer is highly cross linked, the swelling will be very limited, but a polymer containing only a few cross links may take up a large amount of solvent to form a gel.

Gels are rigid structures containing a large proportion of a liquid. They may be relatively weak and easily deformable like common food jellies, or they may be tough and rubbery. Most colloidal systems met with in biology are gels in which water is the solvent phase.

In order that a gel may have a rigid structure it is necessary that the solid component extend continuously through the system. Loosely cross-linked high polymers, when swollen with solvent, represent one type of gel and, since the solid structure is continuously bonded by covalent bonds, the gel cannot be dissolved or melted.

The copolymer of ethylene glycol and glycerine, described on page 117, is an example of a substance which would produce a covalently cross-linked gel. This polymer would swell in water but the extent of the swelling would be limited by the cross linkages at the glycerine molecules. Much weaker bonds between linear polymers will also produce gels. Hydrogen bonds or even molecular friction may be sufficient. In these cases, however, the gel usually dissolves on dilution and can frequently be melted since an increase in temperature usually increases the thermal motion of the chains more than it increases the attractive forces between the chains. Gelatine, agar, and pectin gels are examples of this type of gel.

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[3] S. Palit, *J. Chem. Education* **23**, 182 (1946); and *Ind. and Eng. Chem. Anal. Ed.* **18**, 246 (1946).

A few exceptional solutions form gels on heating; for example, methylcellulose in water, or nitrocellulose in acetone at low temperatures. In these systems the chains attract each other more strongly than they attract the solvent molecules when the temperature is raised. Compounds of low molecular weight which exhibit this behavior, such as butyl alcohol, become less miscible with water as the temperature is raised. A high polymer which is dispersed in solution will form a gel when its solubility is reduced, and the chains attract each other more than they attract the solvent molecules.

In very dilute systems linear high polymer molecules tend to curl up, particularly in poor solvents, to reduce their area of contact with the solvent. Each molecule will then behave as a single kinetic unit. As the concentration is increased the high polymer chains associate more and more with their neighbors and assume more extended configurations. Hydrocarbon chains are highly flexible and all linear polymers have some degree of flexibility. When a long molecule is extended the motion of one part of a chain may have no influence on a remote part and kinetically the chain behaves as if it were a group of molecules. The kinetic unit for hydrocarbons is of the order of 30 carbon atoms. Because of this independent behavior of different sections of a chain, the osmotic pressure of a concentrated solution, which is a measure of the number of kinetic units in a liter of solution, may be many times greater than what would be predicted from the number of molecules in the solution. The greater the length of the chain the greater must be the dilution to prevent molecular interaction and insure that the chains will coil up and behave as single kinetic units. Poor solvents produce smaller deviations from ideal behavior than do good solvents because the chains have a greater tendency to curl up and act as a single unit.

Viscosity and Plasticity.—Common liquids with which we are familiar, such as water, alcohol, oil, and glycerine, are perfect fluids in the sense that they respond to any deforming force by flowing. The rate of flow may be small if the force is small but any force produces flow. The statement that a battleship could be towed by a silk ribbon is essentially true, although of course the rate of towing would be exasperatingly slow.

The viscosity of a liquid composed of small molecules is related to the attractive forces between the molecules. The viscosity is a measure of the drag of one layer of molecules on the layers adjacent to it when the layers are moving parallel to each other. The longer the molecules are, the further they will penetrate into other layers and the more drag they will exert. Consequently, even relatively dilute solutions of high polymers have very high viscosities.[4]

High viscosities exist in low molecular weight liquids only if there are special attractive forces between the molecules. Polyhydric alcohols, notably glycerol, and also sugars have very high viscosities in solution or as pure substances in the molten state. The multiple hydroxy groups make possible hydrogen bonds between molecules and produce a pseudo-high-polymeric structure, which is only occasionally broken by thermal motion of the molecules. With increasing temperature, however, the number of bonds broken per second by thermal motion increases and the viscosity falls rapidly. Glass can be considered as a true high polymer composed of silica chains but at its softening point thermal energies are sufficient to cause occasional rupture of even the covalent bonds between silicon and oxygen.

The higher paraffins found in lubricating oil, although not high polymers, since their chain lengths do not exceed 40, have high viscosities because of the interaction of numerous groups having relatively small attractive forces. The large number of interacting groups makes up for the relatively weak attractive forces. In this case also the structure is rapidly disrupted by increasing temperature.

The viscosity of solutions of high polymers, as might be expected, changes very slowly with temperature since the chains exist as permanent entities in the solution. The solutions, however, are usually sticky and subject to evaporation and hence are entirely unsuited for use as lubricants. Most pure high polymers have such high viscosities, because of high intermolecular attraction, that they are virtually solids and are useless as lubricants. Recently, however, polymers based on silica have been produced (see Chapter 7) which are fluid enough to be useful lubricants. These are true high polymers; increasing temperature therefore produces only a slight decrease in viscosity. The fluidity can probably be ascribed to low intermolecular forces between the "silicone" chains.

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[4] See Eyring, H., and Powell, R. E., *Alexander's Colloid Chemistry* **5**, 236 (1944).

Viscosity may be measured by a variety of different types of apparatus. The type which comes nearest to measuring viscosity in terms of the definition of viscosity given on page 29 is the rotating cylinder viscosimeter, Figure 6–6. In this apparatus a cylinder is hung on a torsion wire inside a slightly larger concentric cylinder, with a liquid occupying the space between them. The outer cylinder may be rotated and the twist or torque on the inner cylinder is proportional to the viscosity of the liquid.

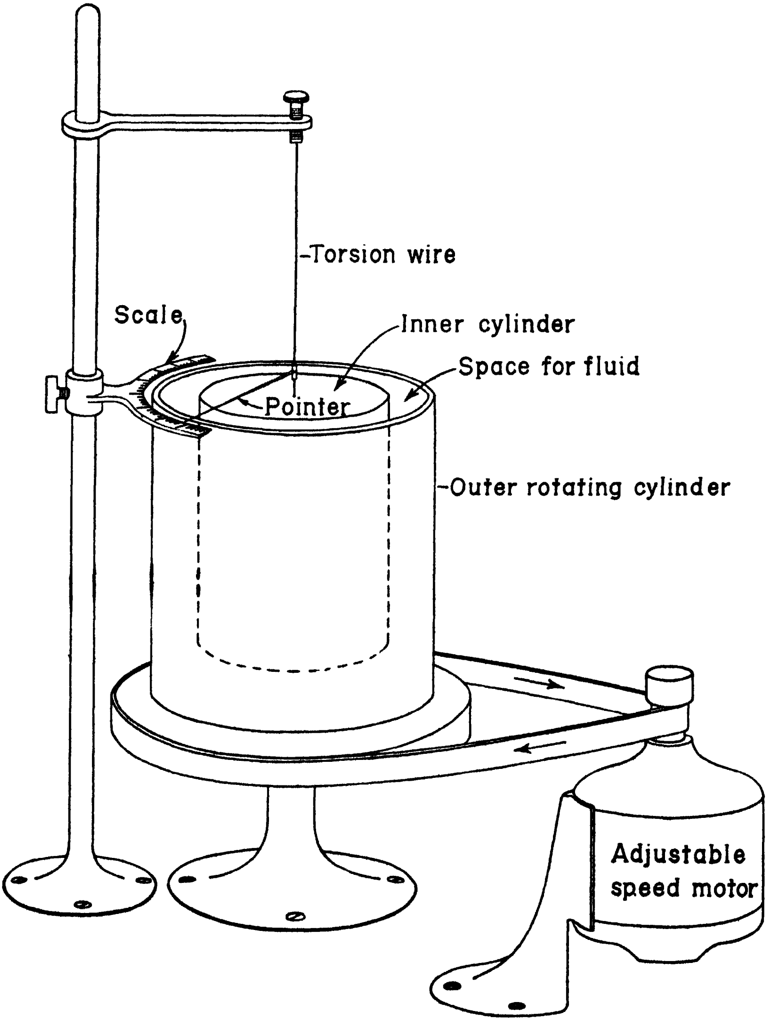

Fig. 6–6. An idealized rotating cylinder viscosimeter.

The Ostwald viscosimeter, Figure 6–7, measures the rate of flow of a liquid through a capillary tube. The time required for a standard volume of liquid to flow between two marks is proportional to the viscosity. The rate of flow of a liquid $\mathcal{Q}$, in cubic centimeters per second through a capillary tube, is given by the following equation,

$$\mathcal{Q} = (P - P_0)\,\pi d^4/128\,L\eta \tag{6–1}$$

where $(P_0 - P)$ is the pressure difference, d is the diameter of the tube and L is its length, and η is the viscosity in poise. Although this equation might be used to calculate the viscosity from the time of flow, it is usual to calibrate capillary viscosimeters by using standard liquids with known viscosities. Since the driving force in an Ostwald viscosimeter is produced by the pressure of a liquid column, the densities of the liquids must also be known. If t_1 and t_2 are the respective times of flow of two liquids having densities d_1 and d_2 the viscosities are related by the following equation,

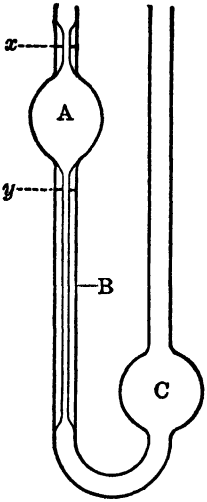

Fig. 6–7. Ostwald Viscosimeter. (From Glasstone, *Textbook of Physical Chemistry*, Van Nostrand (1946).)

$$\eta_1/t_1d_1 = \eta_2/t_2d_2. \tag{6–2}$$

Viscosity can also be measured by the time required for a ball to fall between two marks. Stokes' law (Chapter 2) is used to calculate the viscosity, and a correction should be made for the influence of the walls on the velocity of the ball.

Non-Ideal Fluids.—The resistance to flow of non-ideal liquids is not directly proportional to the velocity of flow. Therefore, viscosimeters which produce varying rates of flow such as occur in a capillary tube or around a falling ball cannot be used. The rotating cylinder viscosimeter, however, submits all the liquid to an almost constant rate of shear. If we fill a rotating cylinder viscosimeter with an ideal liquid and then plot the velocity of rotation of the outer cylinder against the torque on the inner cylinder we will get a straight line through the origin, Figure 6–8, and the slope of the line will be inversely proportional to the viscosity.[5] If a plastic substance is placed in the viscosimeter there may be no flow at all at low torques, but after a certain yield value has been reached the substance will flow.

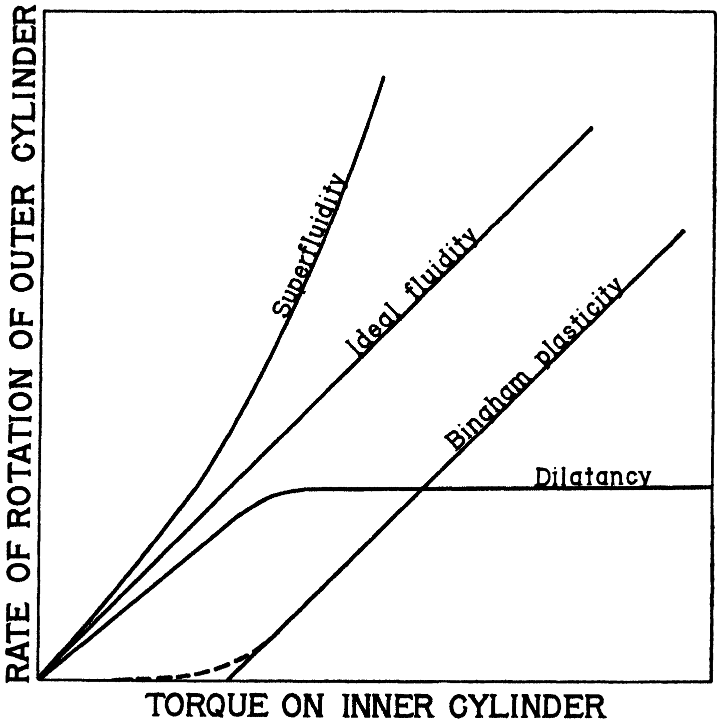

Fig. 6–8. Behavior of fluids in a rotating cylinder viscosimeter.

The behavior of an ideal plastic substance is represented by the line for a Bingham plastic. A Bingham plastic does not flow at low stresses but behaves as an elastic solid. When the stress is increased beyond a critical value, called the yield point, the plastic flows and the rate of flow at higher stresses is proportional to the total stress minus the stress at the yield point. Very few plastic substances are perfect Bingham plastics and the behavior near the yield point is more often represented by the dotted line. There is no simple expression relating the applied force to the rate of flow of a plastic fluid through a capillary.

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[5] Green, H., *J. Applied Physics* **13,** 611 (1942).

Plastic systems are of tremendous industrial and practical importance. Consider the difficulties which would beset a painter if he tried to use an ideal viscous liquid paint on a wall or ceiling. If the paint were an ideal liquid any force would make it flow and the paint would run down the wall and drip from the ceiling before it had time to dry. If the paint were made from a liquid so viscous that there would be no appreciable flow before the paint dried, that paint must either dry too fast to handle or be too thick to stir. On the other hand, a paint which was a plastic fluid can be stirred when the yield value has been exceeded. On a wall in a thin layer the stress due to gravity alone is less than the yield value and the paint would not flow. Modeling clay and paste represent other important types of plastic material. We want modeling clay to yield to our fingers but not to the force of gravity.

Industrially, the term "plastic" is applied to any substance which can be changed from a solid to a liquid and back again to a solid by the application of force and heat. So-called plastic articles are not plastic at room temperature but have been manufactured by heating a solid substance until it could be forced into a mold, and then leaving it in the mold until it became solid. The ordinary plastic substances do not exhibit Bingham plasticity with yield values high enough to be useful. Either the mold must be cooled to harden the plastic before removal or the plastic must be hardened by further chemical reaction in the mold.

Many polymers in solution exhibit a type of plasticity which is termed "super-fluidity" and is illustrated in Figure 6–8. Although there is no yield value the viscosity decreases as the velocity of flow increases. At high velocities the long chains are combed out and oriented more or less parallel to the streamlines, and their interaction with other layers will be less than at low velocities. Thermal motion of the chains is continuously acting to bring the molecules back into a random arrangement, so that at low velocities the long chains exert their influence over a greater distance than is possible at high velocities.

Plastic structure is not always developed rapidly by systems after flow has stopped. The particles in the system may take time to rearrange themselves and to stick together to form a gel structure. Systems which exhibit this phenomenon are called thixotropic. Thixotropic systems when not flowing build up a structure within themselves which is essentially a gel.[5] Application of a sufficient force breaks up this structure and the system flows. When the force is removed particles in the liquid will slowly reassociate to form a gel-like structure once more. Thixotropy is most frequently observed with large flat or elongated rigid particles in suspension. A certain amount of thixotropy rather than true plasticity is also useful in paints since it lets brush-marks flatten out before the paint becomes rigid.

Quite the opposite phenomenon to thixotropy is exhibited by certain systems which increase their resistance to flow as the rate of flow increases. This phenomenon is called dilatancy (see Figure 6–8). Wet sand on the shore frequently exhibits dilatancy in that it appears wet on the surface yet hardens up and dries out when you step on it. If enough water is added to cornstarch to just moisten the whole mass it will be liquid if you stir it slowly, but it will resist rapid stirring. By rapid motion you can mold the paste into a hard ball which appears dry, but if left alone the mass will become moist and flow.

Starch consists of small granules which can fit fairly close together if there is a thin film of liquid around each particle. When the mass is pushed hard the particles jam against each other and form cavities which must be filled by fluid. The fluid is drawn in against the surface tension forces at the open ends of capillary cracks between the particles on the surface. When the stresses on the structure are relaxed the particles readjust into a closer packing and leave excess fluid.

Other systems exhibit dilatancy where it is unlikely that the same explanation holds. Some silicone high polymers have been described as bouncing putty, and elastic silicate putties have also been described by Cole.[6] The elastic silicate made by cautiously diluting commercial waterglass (40% sodium silicate) with 50% alcohol can be worked into a ball that will bounce like a soft rubber ball, but if the ball is left standing on the table it will slowly flatten out into a disk. It is possible that we are here dealing with high polymer chains with many side groups and relatively low intermolecular attractive forces. With slow deforming forces the chains can slide over each other aided by thermal motion of the chains to lift them over the humps. A force applied rapidly would jam the chains and the substance would act as a solid or rubbery elastic body.

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[5] Green, H., and Weltmann, R. N., *Alexander's Colloid Chemistry* **6,** 328 (1946).

[6] J. W. Cole, *J. Chem. Education* **23,** 97 (1946).

Staudinger's Viscosity "Law."—The viscosity of solutions of high polymers, measured at the same weight concentration, increases with increasing length of chain, as has been noted earlier. Staudinger proposed an equation which gives the increase in relative viscosity in terms of the molecular weight of a high polymer.

$$(\eta/\eta_0) - 1 = KMC = \eta_{sp}. \qquad (6\text{–}3)$$

In this equation η is the viscosity of the solution and η_0 the viscosity of the pure solvent. The quotient, η/η_0, is the relative viscosity, η_r, which is measured directly in a capillary viscosimeter. The term $(\eta/\eta_0) - 1$ is called the specific viscosity η_{sp}. The specific viscosity changes with concentration, and Staudinger's law is most nearly true if we extrapolate the measurements to zero concentration. The specific viscosity at zero concentration is, of course, zero but the quotient η_{sp}/c does not become zero but approaches as a limit the intrinsic viscosity $[\eta]$.[7] In terms of the intrinsic viscosity Staudinger's law would be written

$$[\eta] = KM. \qquad (6\text{–}4)$$

The value of the coefficient K is found to depend only slightly on the molecular weight, M. Thus, if the viscosity is known for one sample of known molecular weight, Staudinger's equation permits one to make a fair estimate of the molecular weight of other samples. If C is expressed in terms of the gram atoms of chain length per liter of solution, the values of K vary within a factor of 2 either way from 0.00012. For example, the gram atomic weight per unit of chain length for polyethylene glycol $(\text{—CH}_2\text{—CH}_2\text{O—})_n$ is 44/3 or 14.7. The molecular weight of a solution containing 1.47 gm per liter of polyethylene glycol ought to be about

$$M = (\eta_r - 1)/0.0001 \times 0.1.$$

If the relative viscosity, η_r, of this solution were 1.1, the molecular weight would be of the order of 1000.

Staudinger's equation was derived on the assumption of relatively rigid rods which swept out a volume proportional to the square of their length. This theory is incompatible with our modern knowledge of chemical bonds. The chains of most high polymers are very flexible because of the free rotation possible around any single bond not bound in a ring. Under more rigid experimental examination Staudinger's equation breaks down and the viscosity is found to increase less rapidly than the chain length. Various modifications of this equation have been suggested, but the original equation retains its value as a rapid method for obtaining a first approximation to the molecular weight of a new product. From a practical point of view the viscosity of a high polymer is a property so closely correlated with other desired properties such as strength, elasticity, spinning ability and toughness that it is the one method most frequently used in routine analysis of industrial plastics.

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[7] Crag, L. H., *J. Colloid Sci.* 1, 261 (1946).

Plasticizers.—Many pure high polymers are undesirably hard and brittle because of strong intermolecular forces which hold the chains together in a rigid structure. Any substance which makes a high polymer softer and less brittle is called a plasticizer. Most commercial plasticizers are nonvolatile, small molecules which are soluble in the high polymer.

Plasticizers may function in several different ways. Their primary purpose appears to be separation of the chains, with a consequent reduction in attractive forces between the chains. Solvent molecules will be attracted to the chains and will separate the chains from each other and reduce the attractive forces between chains. The action of solvent plasticizers is frequently very specific as would be expected from the nature of solvent-solute interactions. High polymers which are bound together by hydrogen bonds may be plasticized by esters and ketones which accept the hydrogen bonds from —OH and =NH groups.

A plasticizing effect is often produced by low molecular weight fractions present in the original crude polymer. This was apparently the case with many of the synthetic rubbers. Plasticization can also be produced by the use of mixtures of monomers. For example, vinyl chloride (Chapter 7) forms a hard polymer but a mixture of vinyl chloride and vinyl acetate gives a softer, more useful plastic. This copolymer consists of the two monomer units distributed randomly along the chains. The bulkier acetate radical interferes with the attainment of a regular crystalline alignment and thus reduces the intermolecular attractive forces. (See Fig. 6–9.)

The earliest known plasticizers were camphor and castor oil, both of which are still used to soften cellulose nitrate. Celluloid consists of nitrocellulose containing about 25% camphor as a plasticizer.

Flexible collodion U.S.P. contains 22% camphor and 33% castor oil based on the total nonvolatile material. Other extensively used plasticizers are tricresyl phosphate and dibutyl phthalate. Tricresyl phosphate has exceptionally low volatility and reduces the inflammability of the product, but unfortunately it has a tendency to turn yellow in sunlight. Dibutyl phthalate has good light stability but is more volatile; as a result it slowly escapes from the finished articles, leaving them brittle. Washing with hot soapy water greatly accelerates this loss of plasticizer.

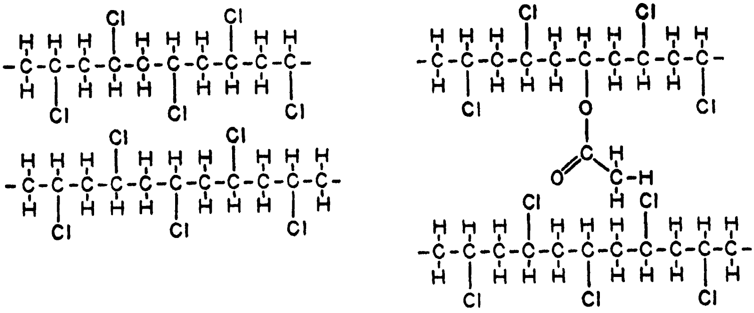

FIG. 6–9.

Nonsolvents, when used as plasticizers, do not greatly reduce the tensile strength of the product and exert a passive lubricating effect. They are prone to "sweat out" and be lost in use. Poor solvents may sometimes be used as extenders for more expensive solvent plasticizers. The good solvent molecules are attracted both to the polymer and to the poor solvent molecules, which are thus anchored in the plastic where they can exert their spacing effect between the chains.

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CHAPTER 7

PLASTICS, RESINS, AND RUBBERS

Thermoplastic Resins.—High polymers which soften on heating are called thermoplastic resins. The softening occurs over a temperature range from 10° to 50° C., depending on the substance, and the softening curve may extend down to room temperatures in some cases. Such plastics exhibit "creep" or "cold flow"—an undesirable property. Even at high temperatures the viscosities of molten plastics are extremely high, and molding machinery must exert pressures of the order of tons per square inch to make the plastic flow into the mold. The softening temperature of typical thermoplastics, measured by one of several arbitrary standard methods, lies between 60° and 200° C. Practical molding temperatures are from 10° to 100° higher.

Thermoplastic resins consist of essentially linear high polymers, which may or may not have short side chains but which contain little or no cross linkage. Even small amounts of cross linkage between chains will produce a gel when the polymer is dissolved in a suitable solvent. The gel-fraction, which is the fraction not soluble in a good solvent, is sometimes used as an indication of the quality of a thermoplastic material.

Thermoplastic resins, since they consist of linear molecules, will soften when heated and are soluble in suitable solvents (it may be necessary to raise the temperature to bring them into solution). They can easily be cemented together by treatment with solvents; in some cases the monomer itself is a good solvent. Solvents will penetrate between the chains and permit intermingling of the chains from both sides of the joint. When the solvent evaporates the two parts are joined substantially as one piece. If the monomer is used as a solvent it may polymerize in the joint and thus eliminate all traces of volatile material.

Inasmuch as the individual chains of a thermoplastic resin are not joined together by covalent bonds, the application of a stress will make the chains slip over one another. This slippage produces "creep" when thermoplastics are placed under stress. On the other hand, thermoplastics are less brittle than highly cross-linked polymers because the chains can flow and yield to a stress. This flow distributes the stress over many chains at once. Rigidly cross-linked substances are brittle because all the stress falls on one link at a time and each link ruptures in turn. Diamond, which has the most complete cross-linked structure of any substance and which is also the hardest known substance, is very brittle. In general, hardness and resistance to deformation go parallel with brittleness, whereas softness and toughness are associated properties.

Plastics Based on Ethylene.—Ethylene, and its substituted derivatives, polymerize to form saturated high polymers with a continuous carbon chain. This type of polymerization is sometimes called A, activated, or true polymerization (since the percentage composition of the polymer is identical with that of the monomer). Condensation, or C polymerization, takes place with the loss of water or other substances. The mechanism of ethylenic polymerization has been extensively studied and reference should be made to more advanced treatises for a detailed discussion. It will not be out of place, however, to give an over-simplified account of the general theory for the purpose of orientation.

Ethylene derivatives ordinarily require a catalyst to initiate polymerization, although ultraviolet light may serve instead. The catalyst, either a peroxide, metal halide, or oxidation-reduction system, furnishes a free radical or activated molecule R*. This activated molecule adds to one carbon of the ethylenic bond leaving the other carbon as an active atom.

$$R^* + CH_2{=}CH_2 \longrightarrow R{-}CH_2{-}CH_2^*.$$

Additional ethylene molecules add to the terminal active atom in the same way until a high polymer is built up.

$$RCH_2{-}CH_2^* + CH_2{=}CH_2 \longrightarrow R{-}CH_2{-}CH_2{-}CH_2{-}CH_2^* \text{ etc.}$$

The entire length of the chain is made in a comparatively short period of time (a small fraction of a second according to some estimates). The active end of the molecule may cease growing if it encounters an impurity which can react with it and absorb the energy of the active group. Polyhydroxy and polynitro aromatic compounds are very powerful chain-stopping substances, and the presence of a few tenths of a per cent of one of these "inhibitors" effectively prevents polymerization until all of the inhibitor has reacted with active molecules produced by the catalyst. Chain-transfer is also possible, often through the action of a "modifier" molecule which stops one chain and starts another. It should be noted that the so-called catalyst remains in the final product and should correctly be called a chain-initiator rather than a catalyst.

Pure ethylene may be polymerized with difficulty at room temperatures, or above, with the production of relatively short chains. At very high temperatures and pressures a high polymer known commercially as polythene is produced. This is essentially an extremely long paraffinic hydrocarbon with a chain length up to 3000 corresponding to a molecular weight of about 40,000 (see Figure 7–1).

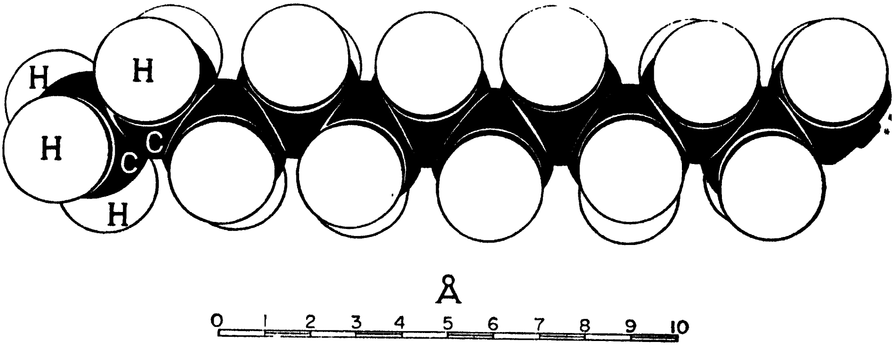


FIG. 7–1. One end of a polythene chain.

Polythene is a tough insoluble plastic that is micro-crystalline. The paraffin chains fit very compactly together in an extended configuration corresponding to the crystals of ordinary paraffin wax. The crystals are not, however, to be thought of as containing whole molecules nor as having flat crystal faces. On the contrary, a single chain may penetrate several crystalline regions as shown in Figure 6–5. The crystallinity cannot be observed by direct optical examination, although it may be inferred from the opacity of the material. X-ray studies, however, indicate quite clearly that the cast polymer consists of numerous randomly oriented crystals with the same spacing between the molecules that is found in paraffin waxes and other paraffin derivatives, such as soaps. If polythene fibers are stretched or "cold drawn," their strength can be increased several fold. Stretching orients the chains, so that a large fraction of them run parallel to the fiber-axis, and increases the crystallinity of the fiber. Both the orientation of the molecules and the increased crystallinity contribute to the tensile strength since the crystalline regions hold the chains more strongly together and prevent slippage. As would be expected, cold drawing also orients the crystallites parallel to the fiber-axis.

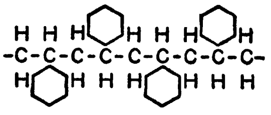
The micro-crystalline structure of polythene also contributes to its high resistance to creep at room temperatures. The crystalline regions effectively anchor the chains that pass through them. The plastic is not hard and brittle, however, since the crystallites can move relative to each other by adjustment of the chains in the inter-crystalline amorphous regions where the chains are randomly oriented.

Polythene, from its essentially paraffinic nature, is resistant to all ordinary organic chemicals although it is swollen by aromatic solvents and their derivatives. Its soft, tough character combined with its chemical inertness makes it ideal for liners for screw-capped bottles. Since it contains no polar groups it has a minimal affinity for water and is therefore nearly impermeable to water vapor even when immersed. This makes it an ideal insulating material for underwater cables.

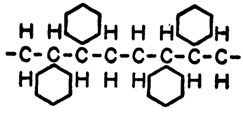
Styrene is a derivative of ethylene with a benzene group substituted for one hydrogen atom, $C_6H_5CH{=}CH_2$. The substituted group greatly enhances the reactivity of the double bond and pure styrene polymerizes slowly even at room temperatures. For that reason it is always supplied with an inhibitor which may be removed by vacuum distillation or by washing. Catalysts, such as benzoyl peroxide, are usually used to speed up the polymerization reaction which may be carried on at temperatures up to 100° C. When styrene or any activated ethylenic compound is polymerized, steps must be taken to remove the heat of polymerization which may otherwise cause overheating. When polymerization nears completion the reaction mass becomes very viscous and can no longer be stirred to bring all parts of it in contact with cooling surfaces. These difficulties can be avoided by polymerizing in aqueous emulsions stabilized by soaps or other detergents. Each emulsion droplet becomes its own reaction vessel and the small dimensions of the drops and the high fluidity of the water phase insures adequate temperature control.

If an attempt is made to produce castings by permitting styrene, or any other monomer, to polymerize in the mold, allowance must be made for shrinkage. Two individual molecules can never approach as close to each other as can two atoms of the same molecule. The two carbons in a paraffin chain are spaced about 1.55 Å apart, but the center of one ethylene carbon atom cannot approach closer than about 3 Å to the center of another ethylene carbon. As a result, when ethylene, styrene, or any other derivative polymerizes, there is a reduction in volume which may be as great as one fourth in the case of polystyrene. This results in the formation of shrinkage holes or bubbles in the casting unless an excess of monomer is supplied.

Polystyrene has no tendency to crystallize and hence is optically clear. The opacity of micro-crystalline materials is due to the greater density and higher refractive index of the crystalline regions. There is some disagreement in the literature as to whether styrene polymerizes in a regular head to tail arrangement,



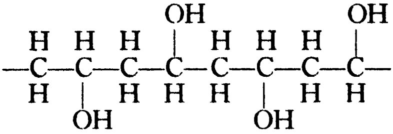
or whether pairs of phenyl groups may occur together as in



In any case the benzene rings are probably sufficiently bulky to make any crystalline arrangement very difficult if not impossible even if the benzene rings were distributed regularly along the chain.

Since it is a pure hydrocarbon, polystyrene has excellent electrical qualities such as high surface resistance and low dielectric loss. It is the preferred substance for mountings of the ultra high-frequency electronic equipment used in radar and television. Polystyrene is also very strong and has high resistance to shock and chemicals except aromatic solvents; in fact its only disadvantages from the point of view of a molding plastic is its high cost.

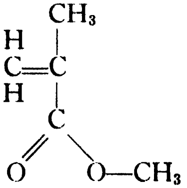
Other ethylene derivatives which are used commercially in the production of plastics include vinyl chloride, $CH_2{=}CHCl$, and vinylidine chloride, $CH_2{=}CCl_2$, which form polymers with properties roughly intermediate between polythene and polystyrene. Vinyl alcohol $CH_2{=}CHOH$ is unknown, but its esters can readily be made by the addition of organic acids to acetylene. Polyvinyl acetate has already been mentioned as forming copolymers with vinyl chloride (Chapter 7). The acetates and higher acid esters of polyvinyl alcohol form tough flexible polymers which are finding extensive use as waterproof fabrics (although they contain no fibers) for molded articles, and for surface coatings such as lacquers for copper wire. Polyvinyl acetate may also be hydrolized to yield polyvinyl alcohol,



$$—\underset{H}{\overset{H}{C}}—\underset{OH}{\overset{H}{C}}—\underset{H}{\overset{H}{C}}—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{H}{C}}—\underset{OH}{\overset{H}{C}}—\underset{H}{\overset{H}{C}}—\underset{H}{\overset{OH}{C}}—$$

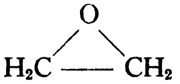
which is a water-soluble substance having many of the properties of starch including the ability to produce blue colors with iodine.

The esters of methacrylic acid, such as methyl methacrylate,

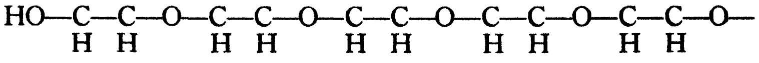


polymerize to form exceptionally clear, transparent plastics which are valuable for their optical properties. The presence of two side groups on every second carbon atom is presumably sufficient to prevent crystallization without reducing strength and hardness unduly. Higher esters of acrylic and methacrylic acids produce polymers which are too soft for use as substitutes for glass. Polymethylmethacrylate, which is known as Lucite or Perspex, is the preferred substance for airplane windows because it can be bent to any shape without loss of transparency. It is also used for dentures to hold false teeth since a mixture of granulated polymer and monomer can be polymerized to a solid mass with only slight shrinkage even at low molding pressures.

Polyethylene Glycol.—One method of making polyethylene glycol by the removal of water from ethylene glycol has been discussed in Chapter 6. This is obviously a condensation reaction and according to some authors should not be called polymerization at all. However, most polyethylene glycol is made up by the polymerization of



ethylene oxide to produce the same final product



$$HO—\underset{H}{\overset{H}{C}}—\underset{H}{\overset{H}{C}}—O—\underset{H}{\overset{H}{C}}—\underset{H}{\overset{H}{C}}—O—\underset{H}{\overset{H}{C}}—\underset{H}{\overset{H}{C}}—O—\underset{H}{\overset{H}{C}}—\underset{H}{\overset{H}{C}}—O—\underset{H}{\overset{H}{C}}—\underset{H}{\overset{H}{C}}—O—$$

(see Figure 6–1).

A trace of water must usually be present as a catalyst and the ends of the chain are occupied by hydroxyl groups. The important point is that the structure of polyethylene oxide, which is produced by a true polymerization reaction, is identical with the structure of the polymer produced by the condensation of ethylene glycol. It is better, as Carothers pointed out, to consider that high polymers include all molecules of high molecular weight which are composed of one or more recurring structural units, regardless of how they have been produced.

The higher polymers of polyethylene glycol are water-soluble waxy substances which have proved especially valuable in emulsions and cosmetic preparations.

Thermosetting Resins.—Thermosetting resins constitute a group of plastics which soften when first heated but which set to a hard infusible resin with further heating. These substances are made from monomers having more than two functional groups per molecule. For example, if ethylene glycol is heated with oxalic acid, it will form long chain polyester molecules. If glycerine is used instead of glycol, each glycerine molecule can start a branch chain. In the early stages of polymerization the mixture will consist of short, branched chains. If the reaction mixture is cooled at this stage, it will produce a glassy solid which is soluble in glacial acetic acid and which can still be melted. Further heat treatment will make the chains link together into a cross-linked super molecule which is hard, brittle, insoluble, and infusible. The extent of polymerization which can take place before the polymer becomes cross linked has been investigated theoretically by Carothers.[1] For the case of equivalent mixtures of a dicarboxylic acid and glycerine, a cross-linked structure will form when 67% to 83% of the active groups have reacted. Carothers, in the same paper, also presented equations giving the average molecular weight of a polymer at any degree of reaction. For linear polymers the average number of monomers per chain is inversely proportional to the fraction of the active groups not yet reacted. Thus, at 90% reaction the average chain will contain 10 monomeric units and at 99% reaction it will contain 100 units.

By far the most important of the thermosetting resins, on a tonnage basis, are resins produced from aromatic phenols condensed with formaldehyde. These resins were first made commercially practical by Leo Baekeland and have been known for years as Bakelite.

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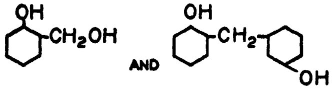
[1] *Trans. Faraday Soc.* **32,** 39 (1936), High Polymers I, p. 408.

Formaldehyde, $H_2C{=}O$, behaves in the presence of water as if it contained some dihydroxy methane, $H_2C(OH)_2$, and is thus a difunctional molecule. Phenol, C_6H_5OH, contains three active hydrogen atoms in the two *ortho* and the *para* positions and is thus trifunctional. When formaldehyde solutions are heated with phenol and a suitable catalyst, products such as



can be isolated together with a large proportion of resinous material of higher molecular weight. Continued heating produces cross-linked polymers similar to those diagrammed in Figure 7–2. The condensation reaction produces water as a bi-product and high pressures are necessary to prevent the formation of steam bubbles. The resin is frequently cooled and granulated before extensive cross linkages have formed and while it is still fusible. Fillers, such as wood flour asbestos, mica or clay, may be incorporated at this stage. The final molding and "cure" of the resin can be carried out when desired. This is frequently done in small manufacturing plants which buy the molding powder ready for use.

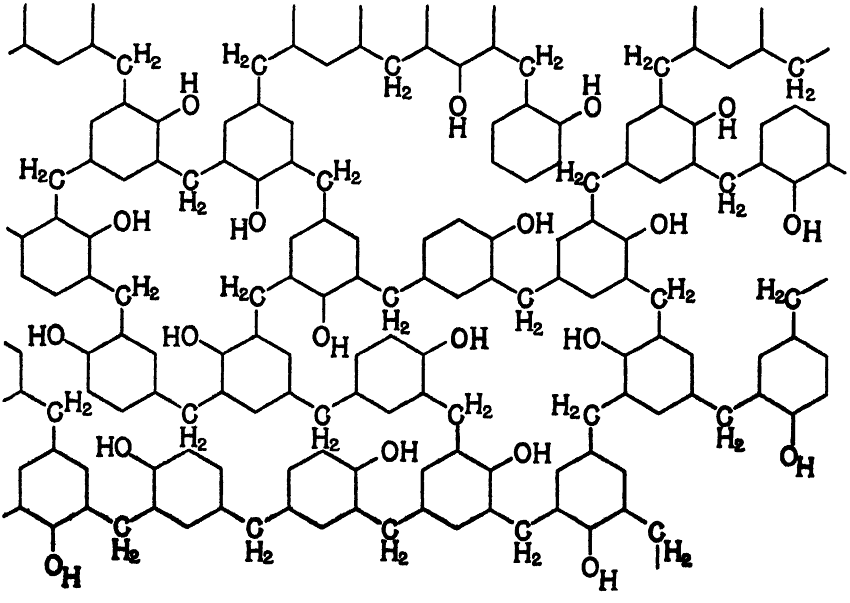
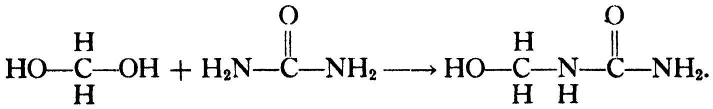


FIG. 7–2. Schematic representation of a cross-linked phenol-formaldehyde polymer.

Other aromatic hydroxy and amino compounds can be used in place of phenol to produce similar resins. Monomers containing *ortho* or *para* substituants, such as *para*-cresol, are difunctional and produce linear polymers only. The commercial advantages of phenol-formaldehyde resins lie in their low cost and rapid molding cycles. Unlike thermoplastic resins which must be cooled in the mold, thermosetting resins can be turned out hot and will not change their shape once cross linkages have been formed and the resin is "cured."

The disadvantages of thermosetting resins lie in their somewhat brittle nature and insolubility, both of which are a direct result of their cross-linked structure. Articles made of thermosetting resins break more easily and are harder to repair than those made from thermoplastic resins. However, the thermoplastics, as their name implies, soften or become plastic when heated and are usually unsuitable for use in boiling water. Phenolic resins have an added disadvantage in that they have dark colors and never wholly lose the odor of phenol.

Many of the physical disadvantages of the phenolic resins are not present in resins made by condensing urea or related products with formaldehyde. Urea, $H_2N{-}C({=}O){-}NH_2$, can condense with formaldehyde as indicated,

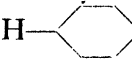


$$\mathrm{HO{-}\overset{H}{\underset{H}{C}}{-}OH} + \mathrm{H_2N{-}\overset{\overset{O}{\|}}{C}{-}NH_2} \longrightarrow \mathrm{HO{-}\overset{H}{\underset{H}{C}}{-}\underset{H}{N}{-}\overset{\overset{O}{\|}}{C}{-}NH_2}.$$

All four hydrogen atoms on urea are potentially able to react with formaldehyde. Urea is thus tetrafunctional and should readily produce highly cross-linked polymers. Urea and formaldehyde in the presence of acid catalysts react rapidly and the mixture quickly sets up to a highly cross-linked polymer. In alkaline mixtures the reaction proceeds more slowly with the formation of soluble and presumably linear polymers. These can be converted to the cross-linked type by the addition of acid (and frequently additional formaldehyde or para-formaldehyde).

The cross-linking reaction can be made to continue even at room temperatures. Urea-formaldehyde glues supplied as powders which contain dry acid catalysts will "set up" shortly after mixing to form a permanently cross-linked high polymer. This glue is especially effective for use on wood since urea-formaldehyde systems form very strong bonds with cellulose. Cotton fabrics impregnated with dilute solutions of the resin and then heated are very resistant to shrinkage and creasing. Somewhat larger amounts of the resin, when applied to cotton, produce results similar to starching with the added advantage that the stiffening is permanent and will not wash out.

Urea-formaldehyde resins are superior to phenolic resins in having practically no color even after aging or exposure to sunlight. They are also odorless and tasteless, but are less resistant to water than phenolics. They share with phenolics all the generic advantages and disadvantages of cross-linked polymers.

Some new developments in commercial plastics combine the good functional properties of both types of resins by the use of a small fraction of a polyfunctional monomer to form copolymers with a difunctional monomer. For example, polystyrene can be converted into a cross-linked polymer by incorporating small amounts of divinyl benzene, $CH_2{=}CH-$$-CH{=}CH_2$ with the styrene before polymerization. By a suitable choice of proportions the final plastic may have the toughness of a thermoplastic and yet be resistant to softening at high temperatures.

High Polymers Used in Paints and Varnishes.—Up until a few years ago all paints and varnishes consisted of a so-called "drying oil" with which might be mixed pigments, resins, and volatile solvents, such as turpentine. The drying oils which form the structure of the final paint are triglycerides of unsaturated fatty acids containing, on the average, two or more double bonds per acid radical. The acids commonly present in domestic oils are linoleic acid with two double bonds and linolenic with three. Even more highly unsaturated fatty acids are present in tung oil and distilled fish oils.

When a drying oil is exposed to the air in a thin layer, it absorbs up to 20% of its weight of oxygen and is thereby transformed into an elastic insoluble film. The complete insolubility of the dried film indicates the formation of a cross-linked high polymer and, although the exact chemical nature of the product is unknown, there is general agreement that the fatty acid radicals are joined together by carbon-carbon or carbon-oxygen linkages. Apparently each fatty acid chain can join to only one other chain because the free fatty acids and their alcohol and glycol esters will not polymerize to make cross-linked insoluble polymers. However, when three fatty acids are esterified with glycerine, as in the naturally occurring drying oils, the resultant molecule is trifunctional and polymerizes with oxygen to give typical cross-linked polymers.

Varnishes and enamels contain some resinous material to give the film gloss and hardness. The naturally occurring resins are esters of heterocyclic organic compounds, and those which are soluble in oils and paint thinners are not high polymers. The application of high polymeric synthetic resins to varnishes and lacquers has followed two rather different lines. Alcohol- and ester-soluble linear high polymers of the type produced by condensing *para* cresol with formaldehyde can, with slight modification of the solvent mixture, be substituted for the natural resins in air-drying varnishes based on drying oils. Some other linear polymers can also be so used.

Synthetic resins, such as phenol-formaldehyde or urea-formaldehyde which are still in the linear stage, may be applied as lacquers in alcoholic solutions and further polymerized on the surface by baking. These coatings are quite suitable for application to rigid metal surfaces, but their highly cross-linked nature renders them brittle and inflexible.

The alkyd resins which form the foundation of our most durable paints consist of polyesters of difunctional acids and polyfunctional alcohols. For baking purposes they may be used alone, but the high proportion of polar groups renders them sensitive to moisture. Very superior finishes are obtained when a polyfunctional alcohol is partially esterified with acids of the drying oil series and then condensed with difunctional acids to form linear polyesters (Figure 7–3). Upon exposure to the air the unsaturated fatty acids undergo further polymerization with the formation of cross-linked high polymers. Pentaerythritol, $C(CH_2OH)_4$, a tetrafunctional alcohol, is superior to glycerine since it permits the attachment by chemical bonds of more than one fatty acid radical per alcohol molecule. The most commonly used dibasic acids are phthalic (used as the anhydride) and malic, both of which may be prepared by oxidation of aromatic compounds.

Many quick drying lacquers and enamels are made by simply dissolving linear polymers in a solvent with suitable pigments. Cellulose derivatives are outstanding in this field. A lacquer of this type forms on evaporation a surface film of entangled linear chains. Pigment particles, if present, may sorb the chains serving as points of attachment for many chains and producing a kind of cross-linked structure. The structure produced in this way is not as permanent as chemical cross-linkages, and solvents readily soften and dissolve the film.

Chemically cross-linked surface films, such as are produced by drying oils, are of course insoluble in any solvent which does not

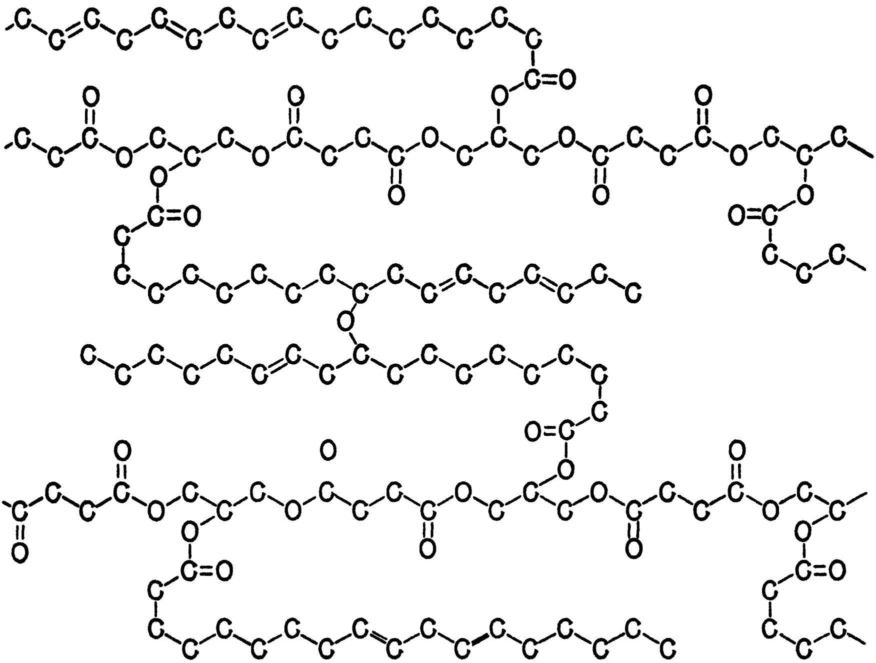


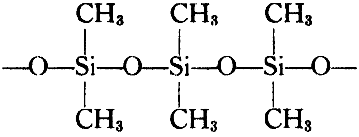
FIG. 7–3. Schematic representation of a glyptal resin.

attack the chemical linkages. However, the ester linkages are readily hydrolized (or saponified) by alkaline solutions which accordingly act as efficient paint removers. Since aqueous alkaline solutions also swell and attack wood, these solutions are not satisfactory paint removers for use on woodwork.

Although cross-linked paint films are not soluble, their structure is loose enough to permit solvent molecules to penetrate between the chains. Good solvents accordingly will make a paint film swell and soften so that it may readily be scraped off. Paints consist of ester groups together with relatively long hydrocarbon chains and accordingly a mixed solvent might be expected to be superior to any simple solvent. You can make a very effective "paint remover" from a mixture of an aromatic solvent, such as benzene or toluene, with acetone or isopropyl alcohol. Many commercial paint removers also contain a wax which is intended to reduce the rate of evaporation and give the solvent time to penetrate the film.

"Silicone" Polymers.—Silica lies immediately below carbon in the periodic table and might be expected to produce a series of compounds similar to the organic compounds of carbon. While there are several silicon compounds which are analogous to carbon compounds, they possess rather different properties. In the first place Si—Si bonds are much weaker than C—C bonds and long chains of silicon atoms are unstable. In the second place compounds of silicon with halides or hydrogen are readily hydrolyzed by water.

Silicon tetrachloride hydrolyzes rapidly in water to form first ortho-silicic acid, $Si(OH)_4$, which then loses water and polymerizes to a cross-linked polymer of amorphous silica, $SiO_2\,x\,H_2O$ (see Chapter 11). If dimethyl silicon dichloride is treated with water, it forms first $(CH_3)_2\,Si(OH)_2$ and this polymerizes to form a linear high polymer



$$\begin{array}{ccccccccccc} & & CH_3 & & & & CH_3 & & & & CH_3 \\ & & | & & & & | & & & & | \\ -O- & & Si & & -O- & & Si & & -O- & & Si & -O- \\ & & | & & & & | & & & & | \\ & & CH_3 & & & & CH_3 & & & & CH_3 \end{array}$$

Other groups may be substituted for the methyl groups but so long as the monomer contains only two halide atoms it is difunctional and produces linear polymers. These polymers have been called "silicones" since their empirical formula R_2SiO is analogous to the formula for a ketone. Actually they are polyethers and the term "silicone" is now used in a loose sense to cover all high polymers containing silicon.

When some of the monomer molecules contain three halide atoms they are trifunctional and capable of binding the polymer chains together as a cross-linked high polymer.

"Silicones" are characterized by having relatively low intermolecular attractive forces. The lower members are oils whose viscosity is relatively insensitive to temperature. They are also characterized by high thermal resistance. Most products are unaffected by temperatures up to 200° C. Thermosetting lacquers based on silicone polymers can be used at higher temperatures than ordinary lacquers. Electric motors insulated with silicone lacquers can be operated at a higher temperature and hence can carry more load and do more work than an ordinary motor of the same size. An additional advantage of silicone lacquers is that when they decompose at high temperatures they leave a fluffy mass of silica which still has insulating qualities, whereas organic lacquers leave a mass of carbon which is a conductor of electricity.

Very rapid advances in "silicone" chemistry have been made since 1940 but many of the results are still restricted information because of their military value.

Rubbers.—The term rubber, as it is used at present, refers to any compound which has long range elasticity. A good sample of vulcanized rubber can be stretched to more than ten times its original length and has a breaking strength nearly as great as silk or nylon fibers and comparable with many metals.

Rubbery properties are shown by a wide variety of organic substances including hydrocarbons, esters, sulfides and elementary sulfur itself. The principal requirement which must be satisfied, if a substance is to exhibit the properties of a rubber, is that it must exist in long chains which do not have high lateral cohesion between the chains. Since the lateral cohesion is, among other things, a function of the number of points at which the chains touch, any influence which tends to reduce the number of contact points will favor the rubbery state.

Increased temperature is one such influence since it increases the random thermal agitation of the chains. Many linear thermoplastic polymers will pass through a rubbery state before melting if the chains are long enough. Polystyrene is a rubber above its softening temperature (about 130° C.), while natural rubber is a typical thermoplastic resin below −80° C. Among other influences which increase the separation between chains can be included solvents and plasticizers. Polyvinyl chloride is a thermoplastic resin which, when plasticized, shows rubbery properties. Many gels also show typical rubbery properties and the rubbery properties of body tissues are due to the separating effect of solvent water molecules on the protein structure which constitutes the body. Chemical modification is also capable of separating chains and reducing intermolecular cohesion. Polyethylene shows no rubbery properties at room temperature, whereas polyisobutylene, which has two methyl groups on every pair of carbon atoms, shows excellent rubbery properties.

It should be obvious from the above discussion that we cannot say that certain substances are rubbers any more than we can say that certain substances are liquids, or gases, unless we specify the conditions and, particularly, the temperature. The rubbery state corresponds to a fourth physical state which is intermediate between solids and liquids. Very few substances will be capable of existing in all four states, however, since rubbers must be high polymers and as such are not volatile and cannot exist in the gaseous state. Sulfur represents an exception since polymerization to the long chained rubbery state is reversible and at high temperatures sulfur does exist as a gas.

Stretched rubbers can be thought of as substances which are molten in two dimensions but are solid in the third dimension, that is in the direction of the chains. The rubbery state may thus be included with other mesomorphous states including "liquid crystals" which show crystalline order in one or two but not in all three dimensions.

The outstanding physical property of good rubbers which differentiates them from other materials is their great reversible extensibility. Ordinary elastic materials break when stretched only 1 or 2% of their length. Rubbers, as has been indicated, can be reversibly stretched as much as ten times their original length before failing. One thing is obvious—if rubbers consist of long chains, as all their properties indicate, these chains must be coiled or tangled up in the unstretched state. This conclusion is supported by X-ray and other evidence. Unstretched rubber shows no crystalline order whatsoever but stretching produces micro-crystallites and the fraction of the rubber which is in the crystalline state increases with the elongation. When rubber is fully stretched, as many as half of the chains are oriented parallel to each other.

Corresponding to the X-ray evidence for crystallinity is the fact that rubber, when stretched, loses its transparency and becomes translucent. This indicates the formation of crystallites having a higher refractive index than the amorphous regions and hence that the chains are more tightly packed in the crystallites than in the unstretched rubber. Dilatometric measurements, in which rubber is immersed in mercury while it is being stretched, also show that rubber shrinks in volume when it is stretched linearly. This decrease in volume is a result of the fact that the chains fit more closely together in crystalline regions than they do in amorphous regions.

Granted that the stretching of rubber pulls the chains into line, some mechanism must be found to explain the fact that the chains return to their contorted configurations when the tension is released. High polymer chains are flexible by virtue of the fact that rotation around any single bond is virtually free and unhindered at normal temperatures. Furthermore, the angle between any pair of single bonds is about 109° (124° between a single and a double bond). Figure 7–4 shows only one of the possible configurations of a paraffinic chain.

The flexibility of long chain compounds is similar in many ways to the flexibility of a chain of metal links and there is no immediately

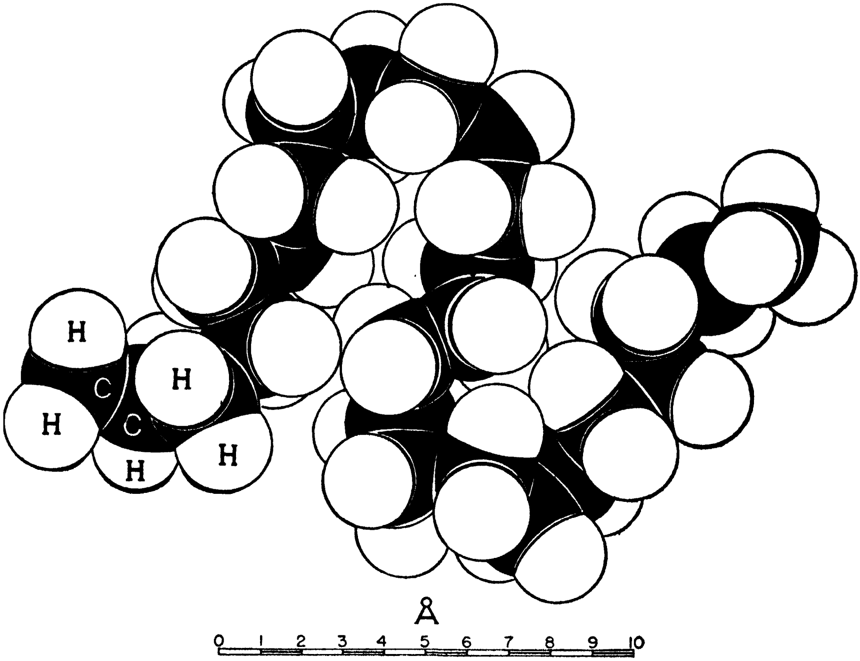


Fig. 7-4. A contorted hydrocarbon chain.

obvious reason why a chain of carbon atoms should curl up once it has been stretched. However, when we consider the detailed behavior of the links of a high polymer, certain effects due to the small size of the units become important. It was pointed out in Chapter 6 that, in concentrated solutions, high polymers behaved osmotically as if they consisted of many small kinetic units moving nearly independently of each other under the influence of thermal energy. The effective length of a kinetic unit is found to be of the order of 30 carbon atoms and each unit will be moving about with a Brownian motion of its own, subject to the restriction that it must remain near the adjacent units of the chain. Each kinetic unit thus has its own 1/2 kT of energy of thermal motion similar to the energy of thermal motion of a gas.

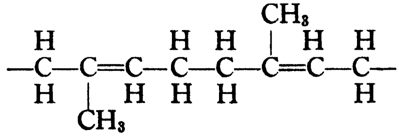
When a rubber is stretched the chain can no longer behave as a collection of nearly independent units and so the thermal energy of these units is lost. This energy appears as heat, and when a rubber band is stretched it does get several degrees warmer. This increase in temperature can most conveniently be demonstrated by touching a rubber band to the lips before and after stretching. Rubber, when it is stretched, gets warmer because the chains have lost some freedom of motion; in the same way a gas gets warmer when it is compressed because there are fewer places where the molecules can go.

When a stretched piece of rubber is released the smaller units of the chain can again move independently of each other and they absorb thermal energy. The absorption of energy by the molecules will lower the temperature of a released band if it is thermally isolated, as it very nearly is in the air. This reversible liberation of heat on stretching is called the Joule effect.

The elasticity of rubber thus appears to be of a type very similar to the elasticity of gases with the important distinction that one is a linear extension with a relatively small decrease in volume, while the other is a homogeneous change of pressure as the volume is decreased. In both cases the system tends to return to the state where it has the greatest number of possible configurations. A contorted chain has many possible configurations for a given distance between its ends whereas a stretched chain has only one possible configuration. Furthermore, the contorted chain may be expected to move through many or all of its possible configurations under the influence of thermal energy. Likewise, gas molecules tend to move out into all available space and lose thermal energy when they are compressed into a fewer number of available positions.

The above treatment of the elasticity of rubbers necessarily represents an extremely simplified presentation of a still controversial subject. Much more precise statements can be made in the language of thermodynamics whereby it can be shown that the entropy of randomly contorted chains is greater than the entropy of chains in the extended state. The Joule effect and the reversible energy of elongation can then be derived from the changes in entropy.

Natural rubber, whether derived from the rubber trees of Brazil and Indonesia or from any of several other rubber producing plants such as guayule or milkweed, is a high polymeric hydrocarbon with the empirical formula C_5H_8 and a chain structure as indicated in the



$$\begin{array}{cccccccc}
 & & & & & \mathrm{CH_3} & & \\
\mathrm{H} & & & \mathrm{H} & \mathrm{H} & | & \mathrm{H} & \mathrm{H} \\
-\mathrm{C} & -\mathrm{C} & =\mathrm{C} & -\mathrm{C} & -\mathrm{C} & -\mathrm{C} & =\mathrm{C} & -\mathrm{C}- \\
\mathrm{H} & | & \mathrm{H} & \mathrm{H} & \mathrm{H} & & & \mathrm{H} \\
 & \mathrm{CH_3} & & & & & &
\end{array}$$

structural formula. Two modifications of the chain are possible depending on the orientation of the double bonds. If all the bonds are *trans*, the structure represents gutta-percha, a plastic with prop-

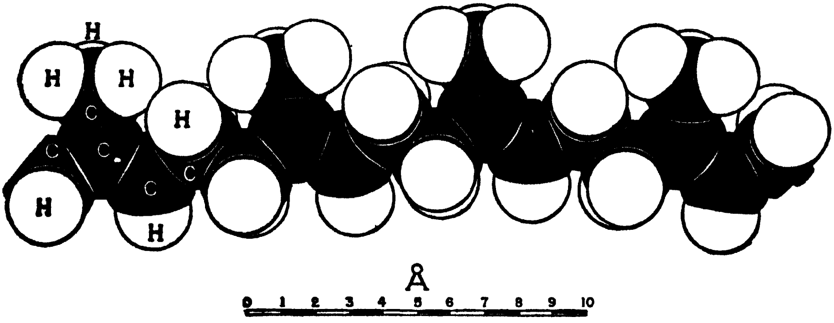


FIG. 7–5. Part of a gutta-percha chain.

erties not greatly different from polythene (see Figure 7–5). Gutta-percha softens to a rubbery plastic at high temperatures but crystallizes readily to a tough horny mass below 50° C.

In natural rubber the double bonds are *cis* and, as can be seen in Figure 7–6, the chains cannot fit tightly together. Consequently the intermolecular cohesion will be lower in rubber than in gutta-percha and we find that raw rubber maintains its rubbery properties down to about 5° C.

Vulcanization.—Natural rubber usually occurs as an emulsion or latex (see Chapter 10) consisting of microscopic particles of rubber in an aqueous plant juice. The latex may be coagulated and the rubber, after it has been dried and, perhaps, smoked, becomes the raw

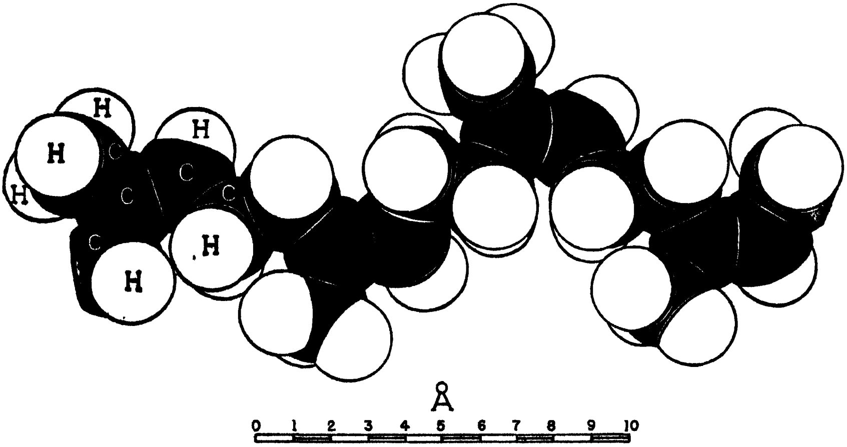


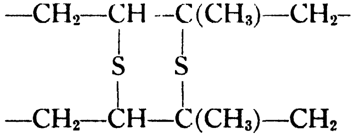
FIG. 7–6. Part of a chain of natural rubber.

rubber of commerce. At room temperatures raw rubber has properties not very different from vulcanized rubber with which we are all familiar. It is a flexible, elastic substance which was used by Charles Macintosh for his early raincoats. Although the early mackintosh was waterproof, it can hardly have been a satisfactory garment. In freezing weather the rubber crystallized and the coat was stiff enough to stand alone. In hot weather the rubber became so sticky and plastic that storage became a serious problem. Furthermore, raw rubber creeps when stretched and a rubber band composed of raw rubber, if stretched around a package, would lose all its tension in a few hours.

Raw rubber is obviously quite unsuited for nearly all of the present-day applications of rubber. The bad properties of the raw substance are due to the fact that raw rubber is a linear polymer and the chains are free to move relative to one another under the influence of tension and thermal motion. All of the failings of natural rubber are eliminated, however, if the chains are tied together to form a cross-linked high polymer. If the cross linkage is not too great and the chains have a length of the order of 100 atoms between links, there will be practically no interference with the thermal motion of the chains which produces the desired rubbery properties. Cross linkages will, however, eliminate creep and by preventing the chains from slipping past each other will greatly increase the tensile strength. Cross linkages prevent the chains in rubber from "melting" and becoming sticky at high temperatures; and, by restricting adjustments between molecules, cross linkages also lower the temperature at which the rubber becomes stiff and brittle.

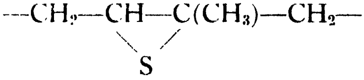
The cross linking of rubber is termed vulcanization, a process which was first discovered by Charles Goodyear in 1839. Nearly a century elapsed between the discovery of the process and reasonable understanding of what takes place when rubber is vulcanized. Even today the exact nature of the chemical bonds in vulcanized rubber is imperfectly understood. Goodyear's vulcanization was by means of sulfur and heat and, with modifications, his method retains its dominance. Other vulcanizing agents have been developed. Some of these contain no sulfur, and others will act in the cold so that neither of the two basic parts of Goodyear's process, sulfur and heat, is necessary for vulcanization.

The changes in the properties of natural rubber which are produced by vulcanization are strong indications that the vulcanizing agents act by joining the chains together with cross linkages. During vulcanization the unsaturation of rubber decreases and the combined sulfur increases in direct proportion to the loss of unsaturation. When rubber is vulcanized with sufficient sulfur to combine with a majority of the double bonds the product is hard rubber or Ebonite, a typical thermoset resin. Much smaller quantities of combined sulfur, as little as one per 100 double bonds, are sufficient to produce satisfactory vulcanization. The exact nature of the bonds produced during vulcanization is still an unsettled question. The majority opinion favors the view that sulfur forms sulfide links between double bonds in adjacent chains.



$$\begin{array}{c} -CH_2-CH-C(CH_3)-CH_2- \\ |\qquad | \\ S\qquad S \\ |\qquad | \\ -CH_2-CH-C(CH_3)-CH_2 \end{array}$$

In any case the mechanism of vulcanization must be fairly complicated since there is little correlation between the amount of bound sulfur and the physical properties. Different accelerating chemicals can produce quite different vulcanized stocks with the same percentage of combined sulfur. This is not surprising when one considers that bound sulfur may remain attached to only one chain as in



$$\begin{array}{c} -CH_2-CH-C(CH_3)-CH_2- \\ \diagdown\;\diagup \\ S \end{array}$$

or it may join two chains together as indicated above.[2]

In addition to rubber and sulfur most rubber goods contain a high proportion of other materials designated as pigments, fillers, and reinforcing agents. Some substances may serve in more than one capacity; carbon black, which is primarily a reinforcing agent, is also a pigment and zinc oxide is used for its combination of pigment and reinforcing actions. Fillers are low-cost inert materials which reduce the cost of articles which will not be subjected to extreme conditions. The behavior of reinforcing agents is worthy of some consideration. The addition of 25 volumes of carbon black to 100 volumes of rubber increases the tensile strength by nearly 50% and reduces the ultimate elongation at break. The finer the particles of carbon black the better it is as a reinforcing agent. The action of reinforcing agents can be compared with the action of pigments in paint films (page 143). Molecular chains of rubber will be strongly sorbed on the surface of the particles and with sufficiently fine particles there is a high probability that a chain will extend between two separate particles. The particles of reinforcing agent will therefore serve as bonds between the chains similar to the bonds produced by vulcanization though of a somewhat different type. The reinforcing agent acts to stiffen the rubber and increase the force necessary to produce a given extension. It also helps reduce abrasion and crack growth.

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[2] See Farmer, E. H., and Shipley, F. W., *J. Polymer Sci.* 1, 293 (1946).

Synthetic Rubbers.—Natural rubber when distilled produces isoprene, $CH_2{=}C(CH_3){-}CH{=}CH_2$, which can also be obtained from turpentine. Isoprene can be made to polymerize as follows:

$$n(CH_2{=}C(CH_3){-}CH{=}CH_2) \longrightarrow ({-}CH_2{-}C(CH_3){=}CH{-}CH_2{-})_n.$$

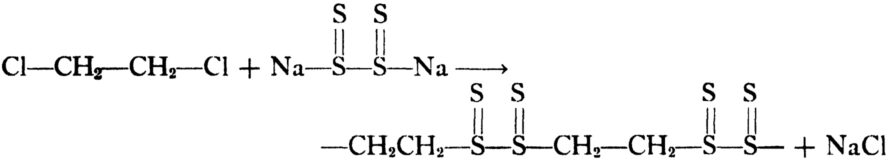
The two conjugated double bonds of the isoprene unit rearrange in polymerization leaving one double bond in the center of the molecule. Polyisoprene has many of the properties of rubber but does not make a satisfactory synthetic rubber. Reasons for the failure of polyisoprene to produce a good rubber are unknown but it is suspected that isoprene does not polymerize in a regular fashion and that many of the resultant double bonds are *trans* rather than *cis*.

Butadiene, $CH_2{=}CH{-}CH{=}CH_2$, resembles isoprene without the methyl group and can be polymerized in the same way to produce a rubber. Much better rubbers are produced if butadiene is copolymerized with styrene or other monomers. The famous GR–S (Government Rubber-Synthetic) of World War II was a copolymer containing six molecules of butadiene to one of styrene. Polymerization was carried out in aqueous emulsions stabilized by soap, much of which was carried through into the final rubber as fatty acids replacing those which would otherwise have been added to the formula. GR–S was a compromise rubber and as a compromise it failed to be thoroughly satisfactory for any given purpose. Its outstanding advantage lay in the fact that it could be manufactured at a time when natural rubber was not available and lack of rubber would have delayed the prosecution of the war.

Polyisobutylene, which has already been mentioned (pages 115, 146), is a chemically saturated rubber, and as such it cannot be vulcanized. However, a copolymer with a few per cent of butadiene contains enough double bonds for vulcanization and, when fully vulcanized, the product is essentially saturated. It is, therefore, much more resistant to chemical attack, particularly oxidation, than are isoprene or butadiene based rubbers.

Chloroprene resembles isoprene but has a chlorine atom replacing the methyl group. When polymerized it produces a rubber, which is called Neoprene (Duprene) and has remarkable resistance to oils which swell and soften natural rubber.

Among the substances which have useful rubber-like properties but which do not resemble natural rubber chemically is Thiokol, an ethylene polysulfide rubber developed by Patrick. Thiokol is a simple condensation polymer made by refluxing ethylene dichloride with sodium tetrasulfide,



$$\mathrm{Cl{-}CH_2{-}CH_2{-}Cl} + \mathrm{Na{-}}\overset{\mathrm{S}}{\overset{\|}{\mathrm{S}}}\mathrm{{-}}\overset{\mathrm{S}}{\overset{\|}{\mathrm{S}}}\mathrm{{-}Na} \longrightarrow$$

$$\mathrm{{-}CH_2CH_2{-}}\overset{\mathrm{S}}{\overset{\|}{\mathrm{S}}}\mathrm{{-}}\overset{\mathrm{S}}{\overset{\|}{\mathrm{S}}}\mathrm{{-}CH_2{-}CH_2{-}}\overset{\mathrm{S}}{\overset{\|}{\mathrm{S}}}\mathrm{{-}}\overset{\mathrm{S}}{\overset{\|}{\mathrm{S}}}\mathrm{{-}} + \mathrm{NaCl}$$

producing sodium chloride as a by-product. The rubber forms a latex in the aqueous system which can be used as a substitute for natural rubber latex in many applications. Apparently at least one sulfur atom in a side grouping is necessary to develop rubbery qualities. The product containing two sulfur atoms per ethylene residue behaves as a plastic, while if three sulfur atoms are present the product is a rubber. Many other groups containing terminal halogen atoms can be substituted for ethylene dichloride to produce rubbers. Thiokol is also resistant to solvents but its chemical nature makes it more sensitive to chemical attack and it is almost impossible to completely remove the odor of hydrogen sulfide from the finished product.

Although a true synthetic rubber has never been produced, in the sense that no synthetic substance exactly reproduces the chemical and physical properties of natural rubber, many substitute rubbers have been produced each one superior in some respect to natural rubber. Research in this direction is going on and, subject to financial considerations, there is no doubt that a whole series of individualized rubbers could be produced just as the steel industry now produces a series of steels for special purposes. Although natural rubber can be delivered at a price well below the cost of present-day synthetic rubber, it has been pointed out that, in terms of man-hours per ton of rubber, the synthetic products require much less labor than natural rubber. If standards of living and labor costs in the rubber growing countries ever become comparable with those in the United States, then synthetic rubbers will be much more economical than the natural product.

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CHAPTER 8

CARBOHYDRATES AND PROTEINS

Cellulose.—Probably the most useful and versatile of all the high polymers is cellulose. Cellulose is the principal substance which gives strength to plant tissues. It takes the place of bones and exoskeletons in the animal kingdom. Cellulose is used in the form of wood for building and fuel, in the form of cotton and linen fibers for clothing, and in the form of paper for a wide variety of purposes. Cellulose is also the structural constituent of ropes, cordage and matting. By chemical action, cellulose can be converted into rayon, Cellophane, celluloid, many plastics and lacquers, and also guncotton.

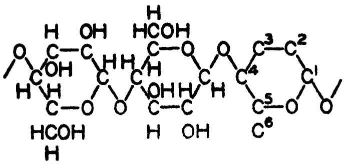


FIG. 8–1. Structural formula of cellulose.

All common plants produce cellulose which is essentially the same chemical substance regardless of its origin. The difference between celluloses produced by different higher plants is almost entirely a difference in chain length and in the arrangement of the chains. Not all plants produce cellulose suitable for use as raw materials for industry. The associated noncellulosic materials include such polymeric substances as resins, waxes and lignins. The removal of the lignins in particular presents great difficulties since these substances are present as a cementing material around the cellulose fibers. The removal of lignin must be carried out under conditions which are deleterious to the cellulose which is being purified. The purest cellulose for chemical purposes is obtained from the boll of the cotton plant, especially from the linters or short fibers which adhere to the cotton seeds. Even this material contains several per cent of fatty substances and pigments which must be removed by treatment with alkalies and chlorine.

Cellulose is a high polymeric carbohydrate composed of glucose molecules linked together by β glucosidal linkages as shown in the accompanying structural formula and in Figure 8–2 which represents the relationships of the atoms in a pair of adjacent cellulose chains.

The empirical formula for cellulose is very nearly $(C_6H_{10}O_5)n$, which is the same as the formula for starch. Starch chains differ from cellulose in being linked by α glucosidal linkages so that all the glucose rings have the same configuration instead of being turned alternately up and down.

The individual chains of cellulose appear irregular in outline but

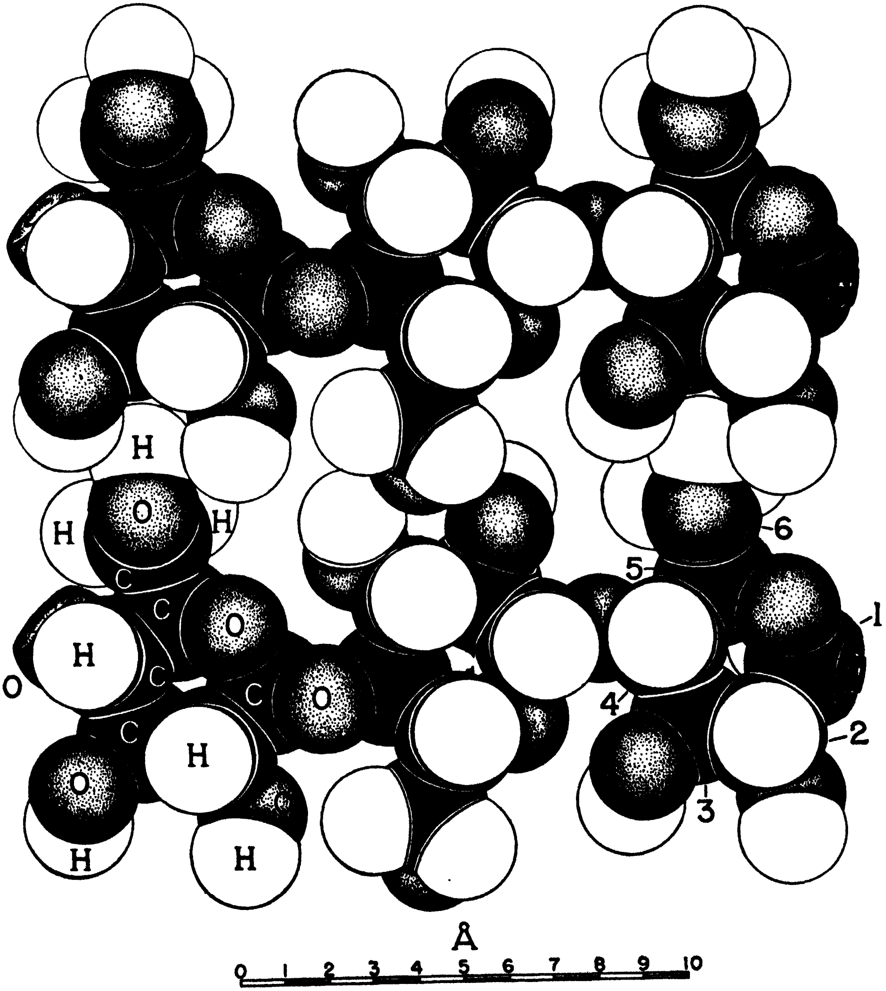


Fig. 8–2. Parts of two adjacent cellulose chains showing hydrogen bonds.

they fit together closely with adjacent chains and there are two possibilities for hydrogen bonding between the hydroxy groups on carbons 2 or 3 of one glucose ring and the hydroxyl on carbon 6 of an adjacent chain. It is undoubtedly the strong interaction of the hydrogen bonds combined with the high molecular weight and relative inflexibility which make cellulose so insoluble in water. Cellulose is, in fact, soluble only in substances which combine with the hydroxy groups and displace the hydrogen bonds that bind the chains together (see pages 162 ff).

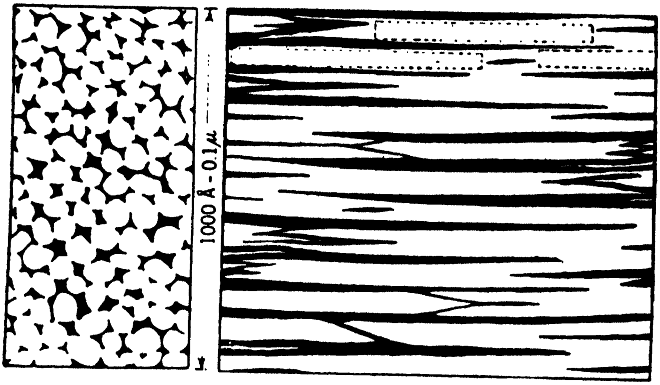


FIG. 8–3. The structure of a cellulose fiber according to Frey-Wyssling. Transverse and longitudinal sections. (From Meyer, *High Polymers* **4**, Interscience (1942).)

The high degree of intermolecular cohesion, and also the possibility of adjacent chains fitting tightly together like two sets of saw-teeth, produce in cellulose a highly crystalline structure. Different samples of cellulose show different degrees of orientation but most good fibers have more than 30% of the cellulose chains in crystalline lattices. As in the case of other micro-crystalline high polymers, the crystalline regions are not as long as the molecules and one molecule may pass through several crystallites or micelles. The average length of the crystallites is about 600 Å, whereas the molecules may be 10,000 Å long.

Although the spaces between molecules inside a crystallite are much too small to permit other molecules to penetrate, the amorphous regions constitute a highly porous structure of colloidal dimensions. Some idea of the porosity may be gathered from the sorption of water by cellulose. From 3% to 6% of water is sorbed by cellulose with the evolution of heat, and this water is certainly bound by hydrogen bonds to the free hydroxy groups. This amount of sorption is equivalent to one molecule of water on every two to four glucose rings. Some authors have interpreted this to mean that one fourth to one half of the glucose rings are available at the surface of the crystallites or as free chains in the amorphous regions. Figure 8–3 shows a probable arrangement of the bundles of molecules which make up a cellulose fiber. Each bundle contains about 150 chains.

The bundles of molecules are further arranged spirally into cylindrical hollow fibers which, in the cotton ball, may be 0.01 mm in diameter and from 1 to 5 cm long. Cellulose fibers in wood are similar to, but usually much shorter than, the fibers of cotton, linen and hemp.

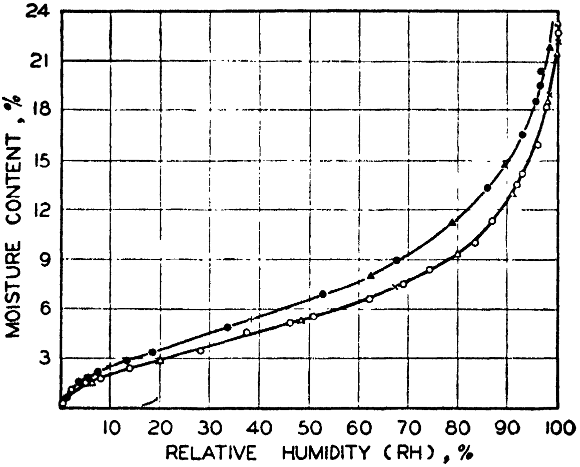


FIG. 8–4. Sorption isotherms of alkali boiled cotton. (From Ott, *High Polymers* 5 Cellulose, Interscience (1943).)

The native cylindrical cellulose fibers of cotton or wood pulp possess only slight attraction for adjacent fibers because their shape permits very small areas of contact. In order to increase the coherence of pulp products, especially paper, it is necessary to beat the fibers, or mascerate them in the presence of water or some other solvent capable of forming hydrogen bonds. The beating action breaks down the fiber into fibrils consisting of several bundles of molecules and greatly increases the possible area of contact between molecules. If beaten pulp is dried out, the fibrils stick together, as in paper, forming hydrogen bonds between adjacent fibrils. Water can re-penetrate between the fibrils, however, separating them, and therefore paper loses its strength when wet by water but not when wet by oils. Water, or some other solvent, which will react to form hydrogen bonds with the hydroxy groups of the cellulose chains must be present if beating is to be effective. In the absence of some good solvent the fibers will coalesce again as rapidly as they are pulled apart.

The highly porous nature of cellulose fibers, which consist of pores ranging in diameter from a few micra down to 10 Å or even less, produces a high sorptive capacity. Figure 8–4 shows a typical sorption and desorption isotherm for alkali-cleaned cotton. As has already been indicated, the initial strong sorption of water which proceeds with the evolution of heat, corresponds to the saturation of the exposed hydroxy groups with the formation of hydrogen bonds. The high sorption at high relative humidities undoubtedly represents capillary sorption. The slowly rising middle portion of the curve presumably represents sorption on ether linkages and multilayer formation on the exposed cellulose surfaces. Cellulose fibers swell in water as the water penetrates between the fibrils but the crystalline structure, as indicated by X-ray studies, shows no change (see Figure 8–5). This is proof that water molecules cannot penetrate between the molecules of the crystallites.

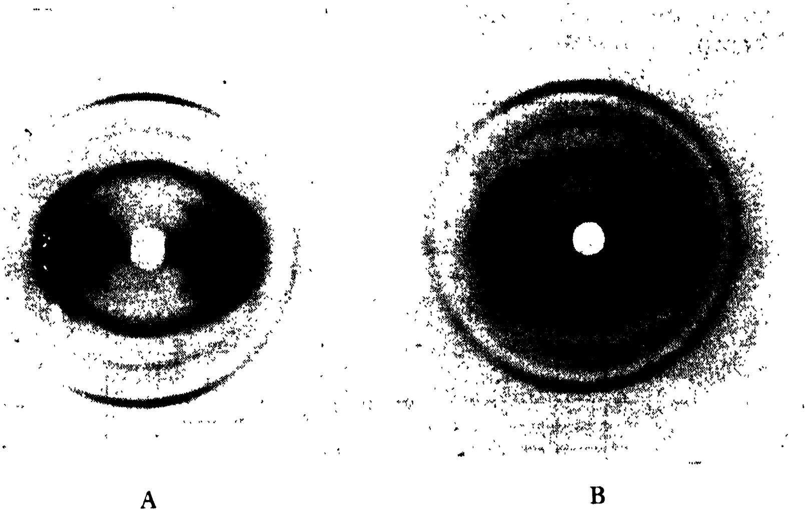


FIG. 8–5. X-ray diffraction pattern of dry cotton fibers (A) and the same fibers soaked in water (B). (Courtesy of E. E. Berkley.)

Although nearly 99% of the cellulose molecule consists of glucose rings arranged as shown in Figure 8–1, other groups also occur.

Even the most carefully purified cellulose contains about 1% of glucuronic acid groups in which the hydroxy group on carbon atom number 6 has been oxidized to a carboxyl as shown in Figure 8–6.

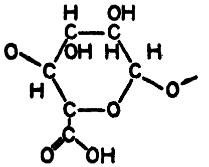


FIG. 8–6. A glucuronic acid.

There are also indications that some of the carboxyl groups may be esterified in the native state with hydroxy groups from other chains or by fatty alcohols. In any case, the alkaline treatment, which is necessary to purify cellulose, always liberates the carboxylate ions which are associated with an equivalent quantity of sodium or calcium counter-ions.

Although the quantity of glucuronic residues in cellulose is too small to produce a detectable change in the carbon-hydrogen ratio, these ionic groups, by virtue of their charge, profoundly modify the behavior of cellulose in dilute aqueous solutions. These negative ions are responsible for the base exchange capacity of cellulose, for the negative zeta potential (Chapter 9), and in part for the sorption of cationic dyes.

In strongly alkaline solution some of the hydroxy groups of cellulose react as acids forming additional negative ions and, when a sufficient fraction has reacted, the cellulose dissolves in the aqueous alkali. Short chain and degraded cellulose molecules are more soluble in alkali than long chain molecules which are arranged in a definite crystal lattice over a substantial part of their length. Alpha cellulose is defined as that fraction of cellulose which is insoluble in cold 18% sodium hydroxide. It corresponds to the fraction which is useful for the manufacture of cellulose derivatives.

When cotton fibers are treated with 18% sodium hydroxide, the fibers swell in thickness and shrink in length. The shrinkage in length may be prevented by keeping the threads under tension. The fibers which result after washing threads treated in this way are known as mercerized cotton. The mercerized fiber shows a slightly different X-ray structure indicating that the molecules have rotated somewhat in the crystal lattice. They also have an increased luster, which may be ascribed to the migration of molecules in the amorphous regions to fill up the spaces between fibrils, and make a more compact fiber. The native fiber contains many submicroscopic cracks which scatter light and give cellulose its dead-white appearance. Mercerization produces a smooth fiber which is nearly transparent and has a high luster.

In order to dissolve cellulose it is necessary to break the hydrogen bonds between hydroxy groups by substituting other bonds which are stronger. Water is not strong enough nor are the common alkalies, but a few reagents react reversibly with the hydroxy groups and bring the cellulose molecules into solution.

The most important of these reagents, from a theoretical point of view, is a solution of cupric hydroxide in ammonium-hydroxide. This reagent is most conveniently prepared by the air oxidation of copper metal in solutions of ammonia. The copper ions exist in solution as the tetra-ammino cupric complex ion.

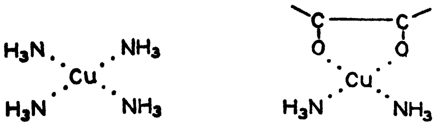
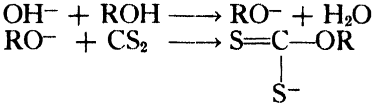


Fig. 8-7. A and B.

They appear to react with the hydroxy groups on carbon atoms 2 and 3 of the glucose ring to form a complex analogous to that formed by copper and tartrates. The two hydroxy groups may ionize as acids neutralizing the charge on the complex ion and liberating ammonia.

The solvent action of copper-ammonia solution is due to the fact that the reagent reacts with the hydroxy groups and loosens the bonds between molecules. The high affinity of the two remaining ammino groups for the solvent also contributes to the solubility of the complex. When copper-ammonia solutions of cellulose are acidified, the cellulose is precipitated, and it is possible to prepare foils or threads of regenerated cellulose by suitable treatment. Although little used commercially, these foils and threads resemble Cellophane and rayon, respectively, and are chemically similar. Copper-ammonia solutions of cellulose find their greatest value in the viscosimetric evaluation of the average chain length or degree of polymerization, DP, which is the number of glucose residues per chain. In the absence of oxygen, copper-ammonia solutions of cellulose do not change in viscosity or DP, although breakdown takes place as soon as oxygen is admitted. Furthermore, a sample of cellulose can be repeatedly dissolved in copper-ammonia solutions and reprecipitated without change in chain length.

The most valuable commercial method for dissolving cellulose is the viscose process. This process depends on the ability of carbon disulfide to form highly ionized soluble xanthates with alcoholates.



$$\begin{aligned} OH^- + ROH &\longrightarrow RO^- + H_2O \\ RO^- + CS_2 &\longrightarrow S{=}\underset{\displaystyle S^-}{\underset{|}{C}}{-}OR \end{aligned}$$

ROH may represent any alcohol including the alcohol groups on cellulose. The solution obtained when cellulose is treated with an alkali and then with carbon disulfide is called viscose. It is an inherently unstable preparation and slowly hydrolyses. The first effect is a drop in viscosity as the cellulose xanthate becomes less soluble due to loss of ionic groups. This fall in viscosity reaches a minimum and the viscosity rises again as the cellulose molecules become still less soluble and stick together. Finally, after about a week, the entire mixture sets to a gel.

Cellulose can be precipitated from viscose solutions by acids. In the preparation of rayon, viscose solutions are pumped through fine spinning jets about 0.1 mm in diameter into a coagulating bath of dilute sulfuric acid. Cellophane is prepared by extruding the viscose solution through a narrow slit into a similar coagulating bath. Commercial Cellophane contains glycerine as a plasticizer and the water-proof varieties have been treated with a cellulose-ester lacquer containing a waxy material. Cellophane, which has not been waterproofed, makes a very satisfactory membrane for ultrafiltration and osmotic pressure measurements. Essentially the same product can be obtained in tubular form (which has been prepared for sausage casings) under the name of Visking. This form is more convenient for dialysis. The pores of regenerated cellulose films are of the order of 10 Å in diameter. It is thus possible to make a partial separation of sucrose from water by ultrafiltering the solution through a Cellophane membrane. The separation is not quantitative since some of the pores are large enough to pass sucrose and even larger molecules. Proteins and other colloidal substances are retained quantitatively by Cellophane or Visking.

The —OH groups of cellulose can form oxonium ions with hydrogen ions and with some other large cations such as Zn^{++} or Li^+. This action is reversible and a high concentration of the reactive ion is necessary since water molecules also compete for positions on these cations. Therefore, only those salts which are highly soluble and those acids which are highly ionized in concentrated solutions will dissolve cellulose. The optimum concentrations for dissolving cellulose appear to be $ZnCl_2$, 65%; HCl, 36%; H_2SO_4, 66%. Paper which has been treated with sulfuric acid is used as a vegetable parchment. The acid produces some hydrolytic breakdown and also forms soluble sulfate esters of the fragments. Upon washing, the breakdown products are reprecipitated between the fibers and cement them together. A similar treatment with zinc chloride is used to prepare "vulcanized fiber" which has exceptional resistance to abrasion and shock.

Cellulose Derivatives.—In addition to the extensive uses of cellulose as it occurs naturally and as regenerated cellulose, there are a number of cellulose derivatives of great commercial importance. Cellulose possesses a ready-made long chain and, by substitution of suitable groups, derivatives can be produced with nearly any desired properties.

Cellulose, and practically all of its derivatives, are linear high polymers and would be expected to be thermoplastic. Cellulose itself is not thermoplastic for the same reason that it does not dissolve in water. The high attractive forces of hydrogen bonds between the chains are not loosened at temperatures below that at which decomposition takes place. The derivatives of cellulose are all formed by chemical reaction with the hydroxy groups. This, of course, eliminates the possibility of hydrogen bond formation, and the resultant products are all soluble and thermoplastic.

The first cellulose derivative to be exploited was the nitrate. The mechanical properties of cellulose nitrate, which has been compounded with camphor to produce celluloid, make it one of the best thermoplastic substances yet produced. Unfortunately, however, cellulose nitrate is highly inflammable and its use is subject to legislative restrictions.

Nitric acid forms nitrate esters of the type $RONO_2$ with alcohols. All three hydroxy groups on each glucose ring of cellulose can be nitrated in this fashion. The formation of esters is a reversible process catalyzed by acids and proceeds to completion only if the water formed in the reaction is removed. For this purpose a mixture of concentrated nitric and sulfuric acids is used. It is very difficult to produce complete nitration of all of the hydroxy groups, and commercial products have from 2 to 2.9 out of every 3 hydroxy groups nitrated.

Guncotton, frequently although incorrectly called nitrocellulose, contains the highest fraction of nitrated groups; approximately nine out of every ten glucose rings are completely nitrated. Nitration appears to be entirely random and there is no distinction between the reactivity of the different hydroxy groups. Explosive grades of nitrocellulose are soluble in acetone and in esters including glycerine trinitrate or nitroglycerine. A gelatinous mixture of nitroglycerine in guncotton is known as blasting gelatine.

Cellulose nitrate which has 2 to 2.5 of the 3 hydroxy groups nitrated (11.1% to 12.7% nitrogen) is soluble in a mixture of absolute alcohol and ethyl ether but is insoluble in pure ethyl ether and only partially soluble in absolute alcohol. This peculiar solubility behavior may be a co-solvency effect. The alcohol may be a solvent for the unreacted hydroxy groups and the ether a solvent for the remainder of the molecule. On the other hand, cellulose trinitrate is insoluble in ethyl ether. It is more probable that the ether serves as a diluent which brings the internal pressure of the solvent closer to that of the solute. A solution of cellulose nitrate in 75% by volume of ethyl ether and 25% absolute ethyl alcohol is known as Collodion. Complete evaporation of the solvent produces foils or membranes containing pores so fine that only water and a few other small molecules can penetrate. If evaporation is stopped by immersing the membrane in water while the film still contains some alcohol, larger pores are produced and it is possible, by suitable control of the drying and washing, to produce pores of any desired size[1] (see also page 28).

Solutions of cellulose nitrate in esters such as butyl acetate are used extensively as lacquers. The long chains present in natural cellulose would produce a viscosity too high for brushing or spraying unless the lacquer is excessively diluted. However, the nitration process itself leads to some cleavage of the cellulose chain and it is customary to permit further oxidative breakdown in alkaline solutions to reduce the viscosity to a workable value. Explosive grade nitrocellulose has a degree of polymerization (DP) of some 3000 glucose units, indicating very little breakdown. Lacquer grades may have a DP as low as 150 to 200. Chains shorter than this do not give enough strength and produce unsatisfactory lacquers. Oxidative breakdown is also practiced in the viscose process and with other cellulose derivatives, since the natural product leads to sys-

[1] Elford, W. J., *Trans. Faraday Soc.* **33**, 1094 (1937).

tems which are too viscous to work economically. Essentially the same type of reaction takes place when rubber is broken down on a mill prior to compounding and vulcanizing.

Cellulose nitrate for use in plastics usually has a DP of about 500 and an average of 2 nitro groups on each glucose ring. Cellulose nitrate is somewhat too hard and brittle for use as a plastic but, when plasticized with camphor or tri-cresyl phosphate, it has excellent molding properties and extreme toughness. Camphor was introduced as the plasticizer of celluloid in 1870 and even today celluloid has the best combination of mechanical properties of any plastic film material. The chief disadvantage of celluloid is its inflammability which produces severe fire hazards in motion-picture projection. Celluloid has not been displaced by other less inflammable products because no other plastic can stand up under the severe mechanical stresses produced by the sprockets of the projection machinery.

The inflammability of cellulose nitrate plastics can be reduced by incorporating flame-resistant plasticizers such as tri-cresyl phosphate or chlorinated hydrocarbons. All cellulose nitrate products are subject to slow decomposition with the release of acidic oxides of nitrogen.

Cellulose acetate, a plastic produced by esterifying cellulose with acetic anhydride in sulfuric acid, has mechanical properties which are nearly as good as celluloid and in addition it does not discolor with age nor is it very inflammable. Cellulose acetate is used, therefore, to make safety film for amateur moving pictures which will not be subjected to as great a mechanical stress as commercial films. Because of its high stability, cellulose acetate is also used for microfilm records. It can also be used to preserve documents according to recent studies of the National Bureau of Standards. For this purpose the document is placed between two pieces of cellulose acetate foil and the sandwich is heated in a press. Under the influence of heat and pressure the cellulose acetate flows into the interstices between the fibers of the paper and welds the whole structure together as one unit. Accelerated aging tests on samples treated in this way indicate that under normal conditions they should last several thousand years.

Cellulose acetate is ordinarily used with about 2.5 acetate groups per glucose ring. At this stage of acetylation it is readily soluble in acetone containing 5% water and is not too brittle. Frequently a mixed ester of acetate and proprionate, or acetate and butyrate, is used. The mixed esters require much less plasticizer than the straight acetate. The higher esters serve as a chemically combined plasticizer in the same way that copolymers of vinyl acetate and vinyl chloride are softer than either pure polymer (page 130).

Cellulose acetate solutions can be extruded to form thin foils similar to Cellophane. When spun as fibers they make an artificial silk known as acetate rayon. Acetate rayon differs from natural rayon and cellulose fibers in that it does not have a porous structure. The amount of dye which can be sorbed on the surface of an acetate rayon fiber is far too little to give it a desirable color. Dyes suitable for use on acetate rayon must therefore be soluble in the cellulose acetate so that they can diffuse in and be distributed through the whole volume of the fiber. Dyes with these properties are available but they are ordinarily soluble only in solvents which swell or dissolve cellulose acetate. Various special methods for dying acetate rayon have thus been devised. One method "solubilizes" the dye in an aqueous detergent solution (Chapter 9). Another method makes use of a water-soluble derivative of the dye which is decomposed in the presence of the fiber. The obvious method of incorporating the dye in the plastic solution before spinning has met with many technical obstacles, but should eventually become the best method for producing solid colors in acetate rayons.

Cellulose ethers, such as methyl and ethyl cellulose, are more recent additions to the family of cellulose plastics. Ethyl cellulose forms unusually clear tough flexible sheets which retain their flexibility down to low temperatures. When highly plasticized, ethyl cellulose has rubber-like qualities which are retained down to −70° C. where rubber products are brittle and glass-like. Ethyl cellulose has a number of other outstanding properties including those which make it very suitable for use in lacquers. As an ether it is more soluble in hydrocarbon solvents than are the esters of cellulose. As in the case of other cellulose derivatives, the solubility and softness are maximal when there are about 2.5 substituted groups per glucose ring.

The solubility of cellulose ethers containing various fractions of the hydroxy groups replaced by ether groups represent an interesting illustration of the laws of solubility. When half of the hydroxy groups have reacted, methyl cellulose is soluble in water. When more than three fourths of the hydroxy groups are substituted, methyl cellulose loses its water solubility and becomes soluble in alcohol and less polar solvents such as chlorinated hydrocarbons.

The fact that hydrocarbon substituants actually increase the water solubility of cellulose may appear to be a paradox, but is in reality readily explicable in terms of the structure of cellulose. Cellulose is insoluble in water because the hydroxy groups form such tight bonds between the molecules that water cannot penetrate. When a fraction of the hydroxy groups is converted to ether groups the molecules can no longer pack closely together and the hydroxy groups cannot form nearly as many hydrogen bonds. As a result water penetrates readily between the molecules and solvates the remaining hydroxy groups. As the fraction of hydroxy groups decreases, the water solubility falls but the substance remains soluble in alcohol which has a lower internal pressure than water. When nearly all of the hydroxy groups have been converted to ether groups, the product is soluble in chlorinated hydrocarbons and aromatic solvents of low polarity.

The peculiar behavior of solutions of methyl cellulose in water, which gel when heated, has already been described (page 122). This property can be put to use in preparation of water-soluble marking inks for glass and porcelain. A solution of a cobalt or iron salt is prepared with enough methyl cellulose to give it a suitable viscosity. Unlike ordinary agents used to increase the viscosity, methyl cellulose does not become more fluid and run when it is heated. On the contrary, it becomes more viscous and sets to a gel from which the solvent water is readily evaporated. Further heating burns out the organic material and fuses the metallic salts into the glass as a permanent pigment.

Methyl cellulose is used as a size for paper and as a water-soluble emulsifying agent replacing natural products like pectin and gum arabic. Other cellulose derivatives of a similar nature have also been produced commercially, in particular hydroxy ethyl cellulose containing $—O—CH_2CH_2OH$ groups and carboxymethyl cellulose containing $—O—CH_2CO_2H$ groups.

Starch.—Starch is probably the most important source of energy in human diets. The major part of the calories of cereals such as wheat, oats, rye and corn, and virtually all of the calories of rice and potatoes, are present as starch. When compared with its use as a food or, after enzymatic breakdown, as a beverage, the quantity of starch which is used for its colloidal properties is insignificant. Even in manufactured foods such as bread, the property of the starch used in the flour is less important than the properties of the associated proteins. The colloidal properties of starch do become important in the preparation of starch puddings, and the use of starch as an adhesive or as a stiffening agent for cotton goods depends primarily on its colloidal nature.

Starch is a high polymer composed of glucose monomers but the glucose rings are joined by α glucosidal linkages. In a structural formula this means that all the glucose rings are turned the same way instead of being alternately up and down as they are in cellulose (Figure 8–1).

Native starches consist of two different starch fractions which are associated together in the starch granules. One fraction, called amylose, or the A-fraction, is a linear polymer with no branches or side chains. The second fraction is called amylopectin, or the B-fraction, and almost always constitutes the larger proportion of the starch. Amylopectin consists of a highly branched polymer. The branches are attached by α glucosidal linkages to the sixth carbon atom of glucose rings. There is evidence to support the supposition that branching is of a dendritic or tree-like nature and that there are no cross linkages. The length of the branches between joints is of the order of 20 to 25 glucose rings. No satisfactory estimates have been made of the size of a native amylopectin molecule, some authors going so far as to suggest that all of the amylopectin in a single starch granule is a single molecule.

Starch granules are insoluble in cold water but swell in water at about 65° C. and eventually burst. Starch is arranged in the granules in concentric layers. The outer layers swell first in hot water and expand tangentially exerting a tension on the inner layers. When starch granules have been swollen in water they become translucent and very viscous. The viscosity is far from ideal and starch pastes owe many of their desired properties to their plastic behavior. The high apparent viscosity of starch solutions is largely structural and a result of the presence of greatly swollen granules of amylopectin which touch each other. Very severe agitation, such as that produced by a mechanical blender, will break up the swollen granules and reduce the apparent viscosity of a starch suspension to a few per cent of its original value.

The amylose or straight chain fraction of starch can be extracted with hot water. The linear molecules slowly diffuse out of the gelatinous mass of swollen amylopectin. This separation is not, however, quantitative and longer amylose molecules tend to remain behind in the gel. Likewise, some of the smaller amylopectin molecules may escape into the amylose fraction.

An improved method for the separation of amylose from amylopectin was developed by Schoch[2] who found that higher alcohols, such as butanol and primary pentanols, cause a selective precipitation of an alcohol-amylose complex which separates as a microcrystalline precipitate. X-ray and optical analysis of the butanol precipitate have shown that the amylose chains form helical coils, presumably around the alcohol molecules. Models of amylose molecules indicate that the molecules can be arranged in a helix containing six glucose rings per turn. In this form there will be fairly strong attractive forces between the glucose rings in adjacent turns. The space inside the turns is large enough to permit the entry of normal hydrocarbon chains and also chains with methyl side groups.

Iodine reacts reversibly with amylose to give a characteristic deep blue color. This reaction is ordinarily carried out in the presence of moisture and iodide ions but is also given by iodine vapor acting on amylose which has been dried from alcoholic solution. Amylose dried from aqueous solutions assumes a dense horny surface which is impermeable to vapors. The blue color of the starch-iodine complex has been attributed to the sorption of the iodine molecules end to end inside the starch helices which are just large enough to accommodate them in this fashion. This linear arrangement of the iodine molecules is a one-dimensional crystalline structure and the iodine would be expected to exhibit the color of crystalline iodine rather than the color of iodine molecules in solution. Further studies have shown that the longer the helix is the greater affinity it has for iodine. Consequently, when iodine is added to a mixture of molecules having different molecular weights, the longest molecules sorb the first iodine until they are full before any of the shorter molecules sorb any iodine at all.

Shorter chains of amylose produce purple or reddish shades, and starch which has been degraded to dextrins containing less than six glucose residues gives no color with iodine. Some of the chains of amylopectin are long enough to produce reddish colors with iodine but the concentration of iodine must be greater than in the case of amylose. For iodometric titrations a starch is desired which gives the maximum color at the lowest concentration of iodine. Degraded starches which give reddish shades spoil the end point. It has recently been suggested that alcohol precipitated amylose in 15% KCl be used as an iodometric indicator. Such a preparation is reputed to be stable and unaffected by microorganisms.[8] Neither amylose nor amylopectin appear to be formed into helices in the starch granule.

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[2] See Kerr, R. W., *Chemistry and Industry of Starch* (1944).

After extraction from the granules, amylose molecules retrograde, as it is called, and eventually precipitate out as a microcrystalline insoluble material. Retrogradation is accompanied by shrinkage in starch pastes and is thus an undesirable property for many technical uses. Fairly concentrated solutions of amylose set to a gel as the molecules cohere at their points of contact. Further coherence leads to retrogradation and eventually crystallization. Amylopectin, with its more highly branched character, is less subject to retrogradation, and glycogen (a starch-like product produced in animals which is even more highly branched than amylopectin) does not gelatinize at all.

Starch may be degraded by the action of heat, acids, or enzymes to produce substances known as dextrins in which the chains are shorter than in the original starch molecules. Dextrins with chains longer than six glucose residues give a red color with iodine and were once known as erythro-dextrins. Shorter chained dextrins which do not give a color with iodine were known as achro-dextrins. Actually dextrins produced by different processes differ greatly in their constitution and properties.

Acid hydrolysis of starch breaks the glucosidal linkages and, if carried far enough, results in the production of glucose. The glucosidal linkages on the sixth carbon atom in amylopectin appear to be more sensitive to hydrolysis, and careful acid hydrolysis of amylopectin results in the production of many short chains corresponding approximately to the units between branches in the original molecule. Dextrins so formed are white and are essentially a low molecular weight starch.

Dry or nearly dry starch when heated turns brown, as is familiar to all who have eaten toast or baked goods. More profound chemical changes take place in the molecule and, in addition to chain clevage, many of the hydroxy groups are bound as ethers or acetals. The chemistry of the heat-treated dextrins is not well understood and is made more difficult by the fact that thermal dextrinization produces a mixture of products.

Starch and its degradation products are used extensively as low-cost adhesives. For adhesive purposes the straight-chain amylose molecules are undesirable because they tend to contract, or retrograde, causing shrinkage and cracking of the seal. A recently developed variety of corn, known as waxy, contains only amylopectin and produces starch with excellent adhesive qualities. Native starch when swollen in water may be used as a viscous paste, but the viscosity is too high for the most economical use. For many adhesive purposes, starch is degraded by alkaline oxidation or by dextrinization.

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[8] Amylose as a 20% paste in butanol is now available from the G. Frederick Smith Chemical Co., Columbus, Ohio.

Starch, like cellulose, can be nitrated and acetylated. Starch nitrate (or nitro-starch) is an explosive. The acetates of starch have been applied as protective coatings and some work has been done on the preparation of starch ethers. Although many of the properties of these starch derivatives resemble the properties of the corresponding cellulose derivatives, the more highly branched structure of starch molecules alters the properties in the direction of greater solubility and reduced strength.

Other Carbohydrate Colloidal Materials.—In addition to starch and cellulose, plants contain a number of other high polymers related to the carbohydrates. Many of these are chemically related to cellulose and occur in conjunction with cellulose. The term "hemicellulose" covers those carbohydrate substances in woody materials which are soluble in alkalies. The term includes low molecular weight molecules identical in all other respects with cellulose, as well as molecules bearing glucuronic acid groups and a series of polysaccharides based on 5 carbon sugars.

Another plant material closely related to the hemi-celluloses is pectin. Pectin is largely present as insoluble proto-pectin in the native state in unripe fruits or lemon-peel. Pectin is extracted from fruits and tubers by mild acid hydrolysis. Soluble pectins are high polymers consisting of galacturonic acid groups which are partially methylated. Pectin is the substance responsible for the formation of a gel in fruit jellies. A solution of sugar, acid and pectin sets to a gel when cooled to room temperature. A pH of about 3.4 and a sugar concentration of 65% to 70% is optimal, and satisfactory jellies can be made which contain only 0.5% of pectin.

The gel-forming properties of pectin depend on a close balance between cohesive forces, which tie the chains together, and the solubility of the rest of the chains. Pectic acid, which is formed from pectin by hydrolysis of the methanol groups, is insoluble in acidic solutions and does not gel. Completely methylated pectin does not gel because it lacks the carboxylic acid groups necessary to tie the chains together. Alcohol precipitates pectin. Sugar, which has alcoholic groups, may reduce the solubility of pectin just enough to let the molecules stick together at a few points forming a gel. It does not lower the solubility to a point where the molecules stick together over most of their length and precipitate out.

Plants contain other water-soluble high polymers derived from cellulose. These all produce viscous sticky solutions and are known loosely as plant gums or mucilages. Agar, a product obtained from certain seaweeds, gels in dilute aqueous solutions and is used for the preparation of bacteriological media, since very few microorganisms possess the enzymes necessary to digest it. Agar is a polymeric carbohydrate containing sulfate esters which are present as the sodium salts. The free acid does not gel. Among the other high polymeric substances based on carbohydrates are alginic acid and its salts, the alginates, from which may be spun rayon-like threads which are water soluble, gum arabic and other water-soluble plant gums such as cherry gum. These are frequently used as protective colloids (see Chapter 10). Most of the properties of these mucilaginous substances are a consequence of their long chain structure which contains many hydrophilic groups.

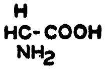
Lignin is an aromatic high polymer of uncertain structure which is found as a cementing material between cellulose fibrils in woody tissues. Most methods for the extraction of lignin produce degradation. The sulfite process for preparing cellulose from wood produces a mixture of sulfonated substances known as lignin sulfonic acid which has detergent and surface-active properties.

Chitin, the structural material of anthropod exoskeletons, is a high polymer composed of acetylated glucosamine units in which the acetylated amino group replaces the hydroxy group on the second carbon atom of glucose. The rings are arranged in the same way as in cellulose and the material, insoluble in all ordinary solvents, may be dissolved in some of the reagents which dissolve cellulose.

Fibrous Proteins and Nylon.—Proteins represent the largest and most diverse group of biological colloids. This chapter will deal only with the insoluble fibrous proteins, the albuminoids or scleroproteins, which include silk, hair, wool, collagen, and the synthetic fiber: Nylon.

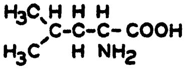
Proteins are high molecular weight substances which, upon hydrolysis, yield a mixture of amino acids. Over thirty amino acids have been identified as constituents of proteins, and reference should be made to any textbook of biochemistry for a complete list. All amino acids which occur naturally are alpha amino acids with the general structure R—CH—(NH$_2$)—COOH. The R group of an amino acid may be polar or non-polar; it may contain additional amino groups or additional carboxyl groups; or it may contain heterocyclic rings. Table 8–1 presents structural formulas of a few

GLYCERIN

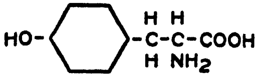


$$\mathrm{H}\overset{\mathrm{H}}{\underset{\mathrm{NH_2}}{\mathrm{C}}}\text{-}\mathrm{COOH}$$

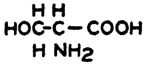
LUCINE



TYROSINE

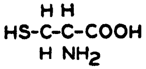


SERINE



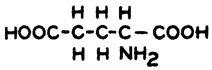
$$\mathrm{HO}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\text{-}\overset{\mathrm{H}}{\underset{\mathrm{NH_2}}{\mathrm{C}}}-\mathrm{COOH}$$

CYSTEINE



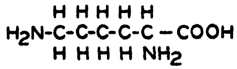
$$\mathrm{HS}\text{-}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\text{-}\overset{\mathrm{H}}{\underset{\mathrm{NH_2}}{\mathrm{C}}}\text{-}\mathrm{COOH}$$

GLUTAMIC ACID



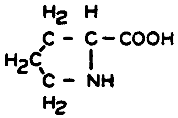
$$\mathrm{HOOC}\text{-}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\text{-}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\text{-}\overset{\mathrm{H}}{\underset{\mathrm{NH_2}}{\mathrm{C}}}-\mathrm{COOH}$$

LYSINE



$$\mathrm{H_2N}\text{-}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\text{-}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\text{-}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\text{-}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\text{-}\overset{\mathrm{H}}{\underset{\mathrm{NH_2}}{\mathrm{C}}}-\mathrm{COOH}$$

PROLINE



amino acids representing the types which are commonly found in proteins. The great variety of amino acids makes possible an incomprehensible number of polymers differing from each other in the proportions of amino acids present and in their arrangement in the polymer. A great variety of proteins has been demonstrated, largely by specific immunological reactions which differentiate between proteins from closely related species of animals or plants.

All proteins are built up of chains of amino acids linked together as amides between the alpha amino group of one molecule and the carboxyl of the next. This linkage is called the peptide link and polymers built up in this way are therefore polypeptides. The term protein is reserved for naturally occurring polypeptides.

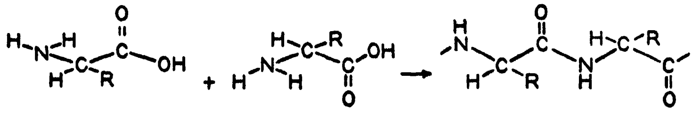


FIG. 8-8.

The formula is shown in a zig-zag arrangement corresponding most closely to the structure of the extended chains which are shown pictorially in Figure 8-9. This figure represents part of a molecule

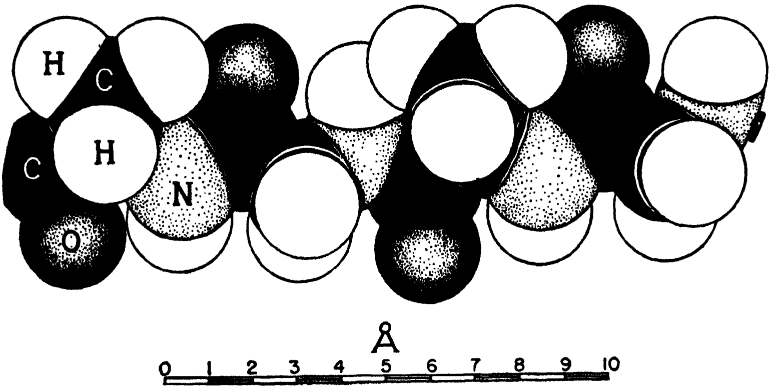
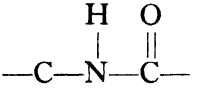


FIG. 8-9. A β keratine chain of glycyl-alanine.

of one of the simplest polypeptides, poly-glycyl-alanine, in which the R groups are alternately —H and —CH_3. The extended planer zig-zag structure is known as the β keratin configuration.

Silk fibroin represents one of the simplest proteins. Silk fibers, as they are spun by the silk worm, consist of a central core of silk fibroin coated with an adhesive material, sericin, which may be removed by boiling in soapy water. The fibroin is in solution as a viscous paste-like material in the silk glands but sets to an insoluble fiber when stretched or extruded. The contents of the silk glands may be extruded by hand, in which case the coarse fiber produced is known as silk worm gut and has been used for fishing line leaders.

Silk fibroin consists primarily of glycine and alanine with smaller quantities of tyrosine and diamino acids. X-ray examination of silk shows it to consist of micro-crystalline regions of oriented poly-glycyl-alanine chains and amorphous regions which must contain the bulkier amino acids. The chains are in an extended β-keratin configuration as represented in Figure 8–9.

Silk is insoluble in ordinary solvents but dissolves in copper-ammonia solutions and other solvents for cellulose. The chains are thus linear with no cross linkages and the insolubility is to be attributed to the very high intermolecular attractive forces. The peptide link  $-\mathrm{C}-\overset{\overset{\mathrm{H}}{|}}{\mathrm{N}}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-$ attracts other peptide links with a bond energy of nearly 12 kilocalories and, in oriented chains, the total cohesive energy will exceed the energy necessary to rupture a covalent bond.

The diamino acids of silk are located in the amorphous regions and hence are available for reactions. In acid solutions they will be present as cations, and silk shows ion-exchange behavior with an equivalent weight of about 4000. This exchange behavior accounts for the affinity of silk for anionic, or acid, dyes.

Silk fibers resemble cellulose fibers in that their strength is a result of orientation and high intermolecular cohesion. Silk, however, does not have a porous structure and the silk fibers as produced by the silkworm are much finer than cellulose fibers. As a result, silk has a soft lustrous appearance combined with high tensile strength in the presence of moisture which has only recently been rivaled by synthetic fibers.

Nylon, which in some respects is superior to silk, is a polyamine containing six carbon atoms between the peptide links. It is made by condensing adipic acid, $HOOC(CH_2)_4COOH$, an oxidation product of cyclohexanol, and hexamethylene diamine $H_2NCH_2(CH_2)_4CH_2NH_2$. These two molecules condense with loss of water to form high polymers. Best results are obtained by spinning the polymer in the molten condition, producing a tough thermoplastic fiber. The strength and sheen of these fibers can be greatly increased by cold-drawing. The original extruded fiber contains chains which are randomly arranged. When the fiber is stretched about 100% the chains are pulled more nearly parallel to each other and the amide groups of adjacent chains help to pull the molecules into a β keratin crystalline lattice. As would be expected, the greatest fiber strengths are obtained in fibers which have the greatest amount of orientation. Nylon has advantages over silk in that a more uniform fiber can be obtained, and there are no extraneous amino acids which increase the water solubility and sensitivity to chemical and micro-biological decomposition. Nylon threads have an elasticity somewhat greater than silk, but they are unfortunately thermoplastic and must not be heated or they will melt. The nonporous nature of the fiber makes it as difficult to dye as acetate rayon. Only dyes soluble in organic solvents are suitable and the techniques used to dye acetate rayon can be also used for Nylon.

Wool, hair, horn, figernails and similar proteins are classified as keratins. Keratins consist of a large number of amino acids including cysteine, and both dicarboxylic and diamino acids. Keratins are insoluble in all reagents which do not attack them chemically. The chains are cross linked by —S—S— groups produced by the oxidation of the —S—H groups of cysteine and in this respect they resemble vulcanized rubber. The —S—S— cross linkages are very easily reduced to —SH groups by alkaline sulfides and these same agents dissolve keratins by rupture of the cross linkages. Keratins are also rapidly hydrolyzed by strongly alkaline solutions.

The protein chain in the keratins appears to exist in a more convoluted form than in silk. Astbury called this convoluted form α keratin and suggested a structure with hydrogen bonds between the $>\mathrm{NH}$ of one amino acid and the $>\mathrm{C{=}O}$ of the next. Astbury's original structure was based only on covalent bond distances and angles and did not take into account the radius of closest approach of atoms which are not covalently bonded. The α keratin structure is now believed to be a wrinkled form of the β keratin with the main chain folded up and down in accordion pleats. Figure 8–10 represents a possible structure for α keratin. See also the paper by Astbury and Bell.[4]

Wool and hair, which normally exist as α keratin, can be stretched when moist to about double their original length. In the stretched state the fibers give an X-ray pattern indicating that the chains are extended, as they are in silk, and in what Astbury calls the β keratin structure. There is little doubt that Figure 8–8 correctly represents this structure. Figure 8–10 represents only one of many convoluted forms which might represent α keratin. As yet we do not know what forces are responsible for the contraction of wool and hair from the β to the α configuration. Silk, with its more regular structure, is converted from an amorphous liquid in the silk glands into a highly oriented crystalline structure merely by stretching, and the process is not reversible at room temperatures.

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[4] W. T. Astbury and F. O. Bell, *Nature* **147**, 696 (1941).

The ability of hair and wool to elongate when moist is made use of in several practical applications. A hair hygrometer consists of one or more hairs attached to a spring with a device for measuring the length of the hair. In moist atmospheres the hair stretches and it shrinks again as it dries. This is in contrast to the behavior of cotton which shrinks in length when wet as the fibrils are pushed apart by swelling in the amorphous regions. Hair or wool, when moistened and stretched or bent, and then dried in the new position, tends to hold its shape so long as it is kept dry. This is the basis of an ironed crease in clothing and of marcel waves in hair.

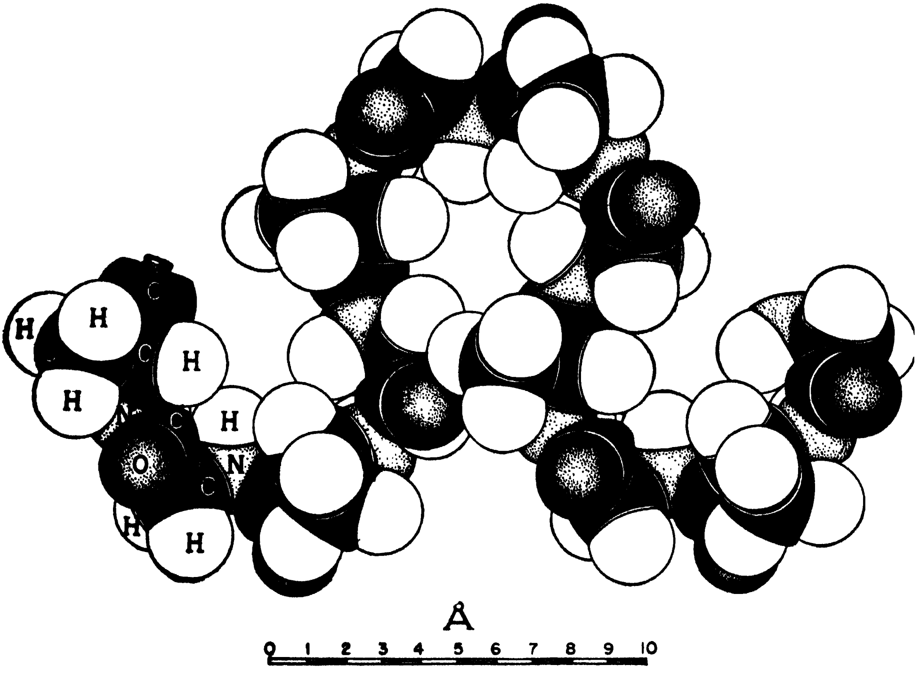

FIG. 8–10. A possible structure of α keratin.

When hair is steamed and stretched for longer periods of time, some of the cross linkages are split and new cross linkages are formed as the hair cools. These new linkages keep the hair in its new shape and the hair is permanently waved. Weak alkaline sulfide solutions rupture a few bonds in the structure of hair and, if the hair is stretched and the reagent is removed, new disulfide bonds form again by air oxidation fixing the hair in its stretched or bent position. This process forms the basis of cold-process permanent waves. Somewhat stronger alkaline sulfides are used as depilatories since they dissolve hair and have but little effect on healthy skin.

The molecular chains in the natural fibers of wool exist in a curled state corresponding to α keratin. This does not appear to be the most stable state because, when the fibers are treated with boiling water, they shrink still further to a super-contracted form which does not give a new X-ray pattern. Strong alkalies, present in impure soaps, loosen the bonds between chains and also produce super-contraction.

Myosin is the principal protein of animal muscles and is responsible for their contractile properties. Myosin fibers in living or dried muscle are present in a convoluted α keratin arrangement. When dried muscle is stretched it can be brought into the β keratin configuration. When living muscle contracts the myosin molecules assume a configuration similar to the super-contracted state of hair and wool. This reversible transformation can take place many hundreds of times a second in the wing muscles of insects.

There is as yet no satisfactory explanation for the contraction of muscle. In many respects muscle resembles rubber. When a passive muscle is stretched it gets warmer, just as rubber does. Actively contracting muscle loses its transparency and scatters light just as a stretched rubber band does. Reference should be made to recent reviews of this fascinating and complicated subject for a more complete exposition of the facts and current theories.[5]

Collagen, the principal protein of hide and tendon, is another form of fibrous protein. The molecular chains in tendons are present in an extended configuration, although there is a large fraction of amorphous material. Hide consists of a felt-like mesh work of collagen fibers enclosing other cellular materials. Collagen fibers swell and lose their strength in water and are attacked by bacteria. When dried the collagen fibers stick together to form a hard horny material known as rawhide. Hide, as it comes from the animal, is thus a most unsatisfactory perishable article. By the process of tanning, however, this unpromising material is converted into a soft, flexible, water-resistant yet porous substance which we call leather.

Tanning agents act by cross linking the molecules in the collagen fibers and saturating the hydrophilic groups so that the fibers will no longer swell in water. Oils are introduced to reduce stiffness, and an excess of tanning material may also function to prevent bacterial action by tanning the proteins in the bacteria.

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[5] Szent-Györgyi, A., *J. Colloid Science* **1**, 1 (1946).

Three types of agents may be used for tanning. Formaldehyde, familiar to all students of zoology, toughens protein materials and renders them resistant to swelling and putrefaction. The formaldehyde appears to form cross linkages between —NH_2 groups of basic amino acids, analogous to the linkages between urea groups in a urea-formaldehyde resin. Some formaldehyde may also react with the =NH groups of the peptide links.

Formaldehyde is used to preserve biological specimens but commercial leathers are never tanned with formaldehyde. Casein, a soluble protein precipitated from milk by acids, can be cross linked by formaldehyde to form a plastic having properties similar to those of urea-formaldehyde resins.

Chrome-tanned leather is produced from hides by the action of chromium salts in acid solution. Chromium salts have a tendency to form complex ions containing —OH, —NH_2, and other groups, for example $[Cr(NH_3)_5H_2O]^{+++}$ (see Chapter 11), and it appears likely that some of the =NH, —NH_2, and —OH groups of the polypeptide chains may enter into complex formation with the chromic ions. On neutralization the chromic complexes form basic insoluble substances which are not soluble in acid solutions. When chromic ions combine with polar groups they eliminate these groups as points of attachment of hydrogen bonds to water. As a result the chromium-tanned collagen fiber will be resistant to swelling by water. If two —NH_2 groups from two different chains were present in the coordination sphere of one chromic ion these two chains would be cross linked at that point.

Vegetable tannins are polymeric glucosides containing several polyhydroxy phenolic groups. These substances are sorbed on hide in acid solution to a very great extent. The hide may increase in weight to four times its initial dry weight by the uptake of tannin, although of course much smaller quantities will protect hide from swelling and putrefaction. The initial uptake of tannin is probably a specific interaction between the phenolic groups of the tannin and some of the polar groups of the leather. Elastic monomolecular films of egg albumin on water are converted into hard rigid films when solutions of tannic acid (purified tannin) are injected into the underlying solution. The multiple phenolic groups on a glucosidal chain act as cross linkages tying together the protein chains on the surface of the water.

Synthetic tannins have been produced which are relatively short chain polymers of benzene and naphthylene sulfonic acids joined by formaldehyde. The nature of the interaction here appears to be a salt linkage between the strong sulfonic acid anions and the $—NH_3^+$ cations formed in acid solution by the second amino group of the diamino acids in the polypeptide chains.

The behavior of proteins in solution will be considered in the next chapter which deals with ionized colloids.

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CHAPTER 9

COLLOIDAL IONS

Globular Proteins.—The structure of the fibrous insoluble proteins has been discussed in the previous chapter and their properties have been compared with the properties of other high polymeric fibers. The properties of a fibrous protein are not critically dependent upon the exact chain length or the molecular weight of the protein molecule. If the chain length were increased from 500 to 2000 atoms, the properties of fibers made from these chains would not be significantly changed. Most of the keratins are cross linked and no useful meaning can be attached to the term chain length or molecular weight of cross-linked polymers.

TABLE 9–1. MOLECULAR WEIGHTS OF SOME SOLUBLE PROTEINS AS DETERMINED BY THE ULTRACENTRIFUGE

Protein	Source	M	f/f_0
Lactalbumin	Cow's milk	17,400	1.1
Gliadin	Wheat	27–28,000	1.6
Lactoglobin	Cow's milk	34–38,000	1.1
Pepsin	Pig's stomach	35–39,000	1.1
Insulin	Pig's pancreas	35,000	1.0
Ovalbumin	Hen's egg	40–44,000	1.1
Hemoglobin	Horse blood	68–69,000	1.2
Serum Albumin	Horse blood	67,000	1.2
Serum Globulin	Horse blood	150,000	1.3
Edestin	Hemp seed	300,000	1.2
Urease	Jack bean	480,000	1.1
Tobacco Mosaic Virus	Tobacco	60,000,000	3.0

The water-soluble proteins are unique among high polymeric substances in that they are remarkably homogeneous with regard to molecular weight. All molecules of a given protein, such as egg albumin, have identical molecular weights and shapes and it is possible to treat them as pure substances, similar in many respects to the crystalloidal substances. A few of the highly purified proteins have been crystallized and appear to form crystals in which the individual molecules retain the shapes they have in solution. Table 9–1 presents molecular weights of a number of purified proteins. The molecular weights quoted in this table may be subject to revisions amounting to 10% or 20% in some cases. This does not mean that different samples of a protein have different molecular weights, but only that the absolute measurement is subject to more error than the relative measurements which have established the fact that all molecules of a given protein have the same size. Most published values of the molecular weights of proteins are presented with more significant figures than the data warrant.

Our knowledge of the molecular weights and dimensions of proteins is due primarily to the outstanding work of Svedberg and his associates with the ultracentrifuge. Many of the determinations of the molecular weight of proteins in solution have been made by means of the sedimentation velocity (see Chapter 2). This method yields results which must be combined with measurements of density, and shape or diffusion coefficient before they can be converted to molecular weights. The sedimentation equilibrium measurements give molecular weights directly but are far more difficult to carry out. Molecular weights up to about 40,000 can also be measured by osmotic pressure methods, and the results obtained are in fair agreement with measurements in the ultracentrifuge.

Most water-soluble proteins are approximately spherical in solution. The departures from a spherical shape are indicated by the dissymmetry number, f/f_0, which measures the resistance to movement of the molecule when compared with the resistance of a sphere of the same volume. The relations between dissymmetry numbers and axial ratio for prolate, or cigar-shaped, ellipsoids and for oblate, or door-knob-shaped, ellipsoids have been calculated.[1] Neither of these calculated shapes is a very probable one for protein molecules, but they are the only shapes for which the dissymmetry ratios can be calculated conveniently. Many spheroidal proteins which have dissymmetry ratios close to unity may exist in box-like shapes with rounded edges and corners.

The globular shape of most water-soluble proteins may be inferred from the low viscosities of their solutions. Serum albumin solutions containing 30% of protein are light, mobile fluids not very much more viscous than water. In contrast, solutions of extended molecules, such as are found in gelatine or myosin, are too viscous to pour at this concentration.

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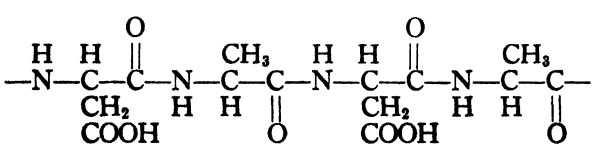
[1] Neurath, H., Cold Spring Harbor Symposium on Quantitative Biology **8**, 85 (1940). See also Polson, A., *Kolloid Zeit.* **88**, 51 (1939).

Egg albumin is a globular protein which has been studied extensively. It has a molecular weight of about 40,000 and the molecules are approximately cubical, each side measuring 40 Å. When a trace of dry egg albumin is placed on the surface of water it spreads to a monomolecular film which is only 10 Å thick. This surface film is insoluble and no longer has the properties of the original egg albumin. The protein has been denatured by spreading at the surface.

The term denaturation is applied rather loosely to any process which converts a globular protein into an extended and frequently insoluble form. Proteins may be denatured by spreading at a surface; by chemicals such as urea, alcohol, or detergents; or by heating. Boiling water denatures and coagulates egg albumin and produces the "white" of a hard-boiled egg. The formation of precipitates of proteins with heavy metals or complex acids is not considered to be denaturation since the precipitating agent is carried down with the protein.[2]

The formation of surface layers only 10 Å thick from protein molecules which are 40 Å in diameter indicates that the molecule must unfold in some way when it is spread on the surface. Further evidence of unfolding is given by the fact that proteins which have been denatured by detergents or urea can be spun into fibers. These fibers can be stretched up to 700% in steam. Stretching orients the chains in the fiber and produces an X-ray fiber pattern resembling that of β keratin. The stretched fibers resemble silk in many respects and consist of long protein chains which have been derived from the globular protein.

The β keratin arrangement of protein chains places the R groups alternately above and below the zig-zag polypeptide backbone. Many of the keratin proteins contain approximately equal numbers of polar and non-polar amino acids. The behavior of these proteins can best be explained if we assume that the polar and non-polar groups are arranged alternately along the chain so that all the polar groups are turned downward and all the non-polar groups are turned upward.



$$\begin{array}{cccccccccccc} & & O & & & & & & O & & & \\ H & H & \| & & CH_3 & & H & H & \| & & CH_3 & \\ -N- & C- & C- & N- & C- & C- & N- & C- & C- & N- & C- & C- \\ & CH_2 & & H & H & \| & & CH_2 & & H & H & \| \\ & COOH & & & & O & & COOH & & & & O \end{array}$$

FIG. 9-1.

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[2] See Neurath, *et al.*, *Chem. Rev.* **34**, 157 (1944).

This structure is represented diagrammatically in Figures 9–1 for a peptide which is composed of alanine and aspartic acid. A picture of the same substance drawn from atomic models is shown in Figure 9–2.

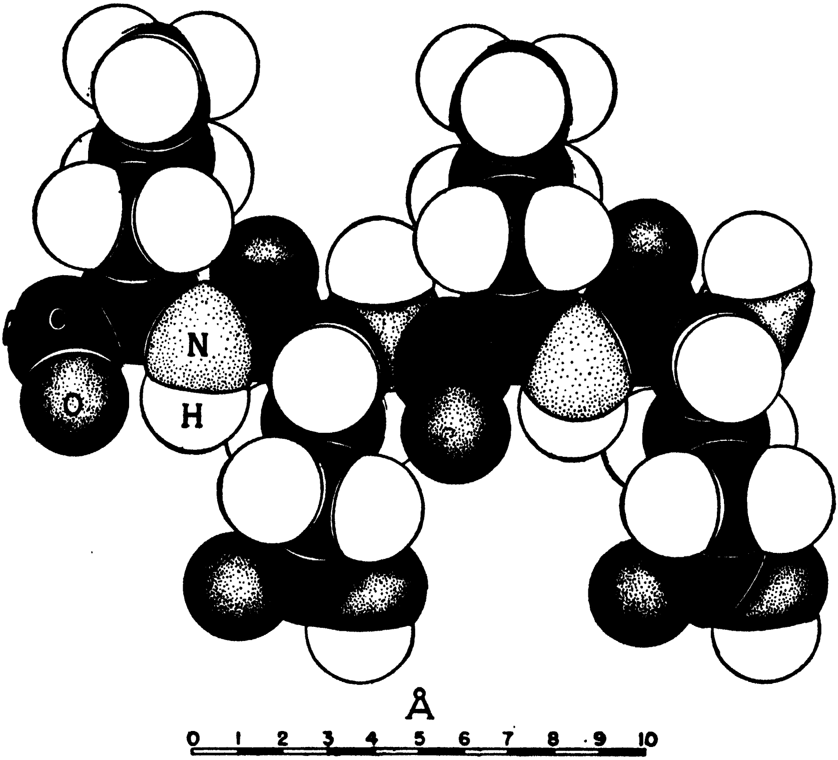

Fig. 9–2. Polypeptide chain in the β keratin configuration.

The molecule of egg albumin may consist of four superimposed layers of polypeptide chains, each layer composed of eight chains having about twelve amino acids per chain. Figure 9–3 according to Palmer[3] represents this structure schematically. The two polar interfaces in the middle of the molecule may be held together by electrostatic attraction or even un-ionized salt linkages. The top and bottom pair of layers may be bound together by occasional —S—S— bonds between oxidized cystein residues, since these residues would be expected to be on the non-polar side of the molecular chains. When a protein is denatured there is an increase in the

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[3] *J. Phys. Chem.* **48**, 15 (1944).

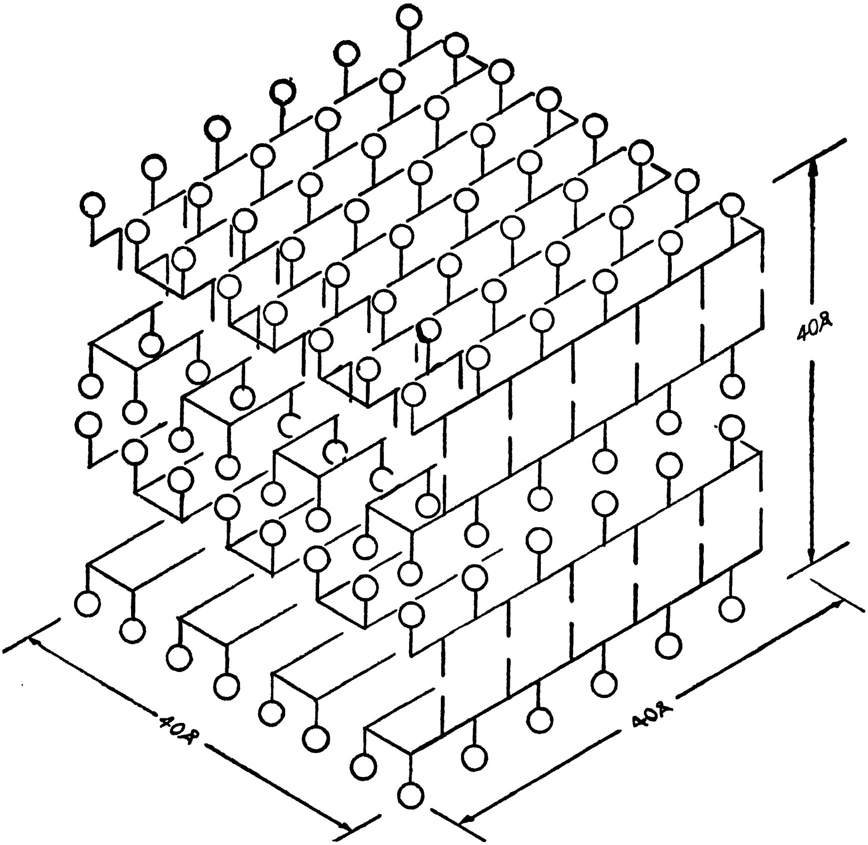
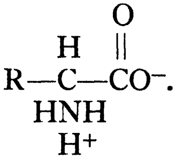


FIG. 9–3. A schematic diagram of a molecule of egg albumin. (Redrawn from K. J. Palmer) *J. Phys. Chemistry* **48** (1944).)

number of available —SH groups. This is what would be expected if the cysteine is present in an oxidized disulfide form in the native protein and these disulfide bonds are opened when the molecule is denatured.

The structure presented here shows how it is possible to convert a globular protein into a surface layer only 10 Å thick. There is probably some uncoiling of the chains in each layer since proteins which are spread on water can be removed in a fibrous form. Denaturation by means of urea or detergents appears to release the chains as independent entities since they can be spun from the denatured solution in the form of fibers in which the chains are extended. It is not yet certain whether the protein molecule consists of one, two, or four peptide chains. In the latter cases the chains are probably attached together by disulfide links or perhaps even by hydrogen bonds between polar groups.

The model of the egg albumin molecule presented in Figure 9–3 is an attempt to account for the properties of the substance in terms of a probable structure. Much still remains to be learned about protein structure, and later developments may alter the picture in many details. In particular we need to know more about the forces which hold the layers together. It should also be remembered that egg albumin is only one of a large number of globular proteins and, furthermore, that there are many more nonglobular proteins about which we know little or nothing.

The Ionization of Proteins in Solution.—The polar side chains on proteins consist of both —COOH groups and —NH_2 groups as well as phenolic and heterocyclic nitrogen groups. When a protein is dissolved in water the carboxyl and amino groups will ionize to produce —COO^- and —NH_3^+ respectively. This behavior is similar to the behavior of ammonium acetate, NH_4OOCCH_3, which is almost completely ionized to NH_4^+ and CH_3COO^- ions. Amino acids show the same behavior except that the two ions are tied together in the same molecule as  $R-\underset{\underset{H^+}{HNH}}{\overset{H}{C}}-\overset{\overset{O}{\|}}{C}O^-$. A molecule such as an amino acid which bears both positive and negative ions is called a zwitter-ion.

When a strong acid is added to ammonium acetate, the hydrogen ions combine with the acetate ions to produce acetic acid leaving the positive ammonium ion in solution. In the same way, the addition of a strong acid to an amino acid or a protein will produce —COOH groups and will leave positive —NH_3^+ ionic groups on the molecule.

Conversely the addition of a strong base produces ammonia from the ammonium ions of ammonium acetate and leaves the negative acetate ion in solution. The addition of a base to an amino acid or protein will produce —NH_2 groups and will leave negative —COO^- ionic groups on the molecule.

We can summarize this behavior by saying that acids leave an excess of positive ions (which are, of course, associated with the negative counter-ions of the acid) and bases leave an excess of negative ions (associated with the positive counter-ions of the base).

It is neither necessary nor probable that a protein or amino acid have exactly the same number of acidic and basic groups. If a molecule has more acidic groups than basic groups, it will have an acidic reaction. Aspartic acid, $HOOC—CH_2—CH(NH_2)—COOH$, when dissolved in water, ionizes to form H^+ and $^-OOC—CH_2—CH(NH_3^+)—COO^-$, a molecule which has two negative groups and one positive group. This molecule will behave as an anion and, in an electric field, will be attracted to the positive pole. The addition of a base to aspartic acid will convert the NH_3^+ ion to $—NH_2$, leaving two negative ionic groups on the molecule. The addition of acid, however, will convert $—COO^-$ ions to $—COOH$ and, if only enough acid is added to convert one of the two $—COO^-$ ions to $COOH$, the resultant molecule will have one positive ion and one negative ion. In an electric field this ion cannot move because the attractive force on the positive ion is equal and opposite to the attractive force on the negative ion.

The ionization of proteins shows a similar behavior but, since there are many positive ions and many negative ions on a single molecule, it is not possible to identify the individual ions. A protein which has equal numbers of positive and negative ions is said to be at its iso-electric point. Since the number of ions of both signs depends upon the acidity, or the pH, of the solution, *the iso-electric point is defined as the pH at which a molecule has equal numbers of positive and negative ions.* At the iso-electric point a molecule will not migrate in an electric field. On the acid side of the iso-electric point it will move toward the negative pole, and on the basic side it will move toward the positive pole. Figure 9–4 shows how the mobility of horse serum albumin in an electric field changes with changes in pH. The iso-electric point is the point at which the velocity is zero. For this preparation the iso-electric point is at pH 4.8.

The iso-electric points of different proteins lie between pH 2 for silk fibroin and pH 12 for the basic protamines from fish sperm. A large number of common proteins have iso-electric points between pH 4.5 and 6.0.

At the iso-electric point the total number of charges on a protein is maximal but the net charge is, by definition, zero. Many of the physical properties of protein solutions have maximal or minimal values at the iso-electric point. In any experimental study of the properties of protein solutions, therefore, it is essential to control the pH. Buffer solutions are ordinarily used for this purpose.

A buffer consists of a solution containing both a weak acid and its salt or a weak base and its salt. Two commonly used buffer systems are (1) acetic acid and sodium acetate between pH 4 and 6, and (2) a mixture of di-hydrogen and mono-hydrogen phosphates between pH 6 and 8. When a little acid is added to the first system some of the acetate ions are converted to acetic acid with a relatively small change in pH. Conversely, when base is added the acetic acid is converted back to acetate ions. The pH of a buffer solution can be calculated from the equation:

$$\text{pH} = \text{pK} + \log(\text{base/acid}) \tag{9-1}$$

where (base/acid) means the concentration of the basic form (which is the acetate ion in case 1) divided by the concentration of the acidic form (which is the acetic acid in case 1). The pK is the negative logarithm of the acidic ionization constant which may be obtained from tables. The pH equals numerically the pK when the acidic and basic forms of the buffer are present in equal concentrations. The pK of acetic acid is 4.8 and the pK's of phosphoric acid are 1.0, 7.1 and 12.3 for the three hydrogen ions. A buffer can be used in a range of about one pH unit on either side of its pK value. More

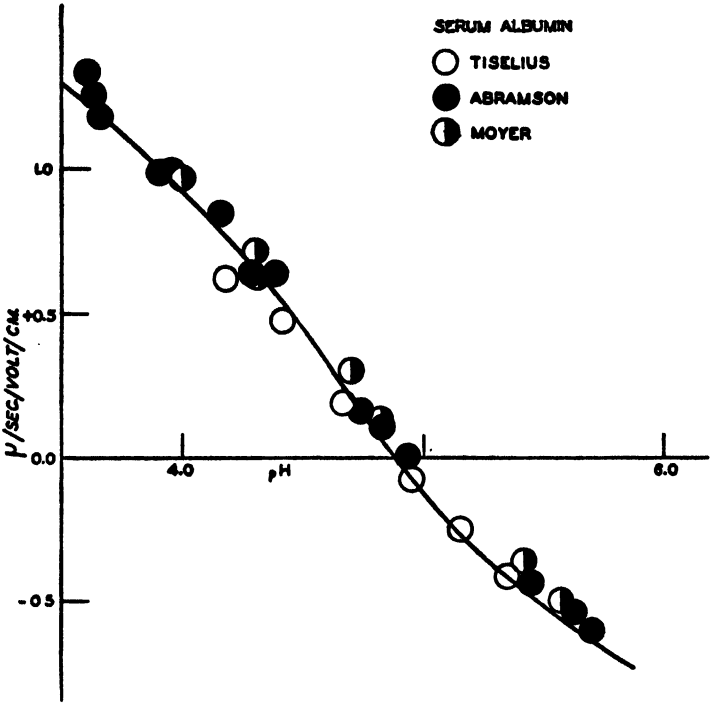


FIG. 9–4. The electrophoretic mobility of horse serum albumin. (From Abramson, Moyer and Gorin, *Electrophoresis of Proteins*, Reinhold (1942).)

extensive expositions of pH and buffer solutions will be found in any textbook of physical chemistry and in most textbooks of analytical and biochemistry.

Solubility and Precipitation of Proteins.—Proteins in solution are precipitated by many heavy metals and complex acids. The poisonous qualities of silver, mercury, copper, and lead salts are due, in part at least, to their ability to precipitate and destroy the proteins of the alimentary tract. It follows that a soluble protein, such as egg white, should be an effective antidote since it will precipitate the poisonous metallic ions which still remain in the stomach.

The nature of the chemical reaction between a precipitating ion and a protein is apt to be very complex. In addition to simple salt formation, the ions of heavy metals may form complexes with the —NH_2 groups of the protein. The RSH groups are also capable of reacting in the same way that hydrogen sulfide, HSH, reacts. The heavy metals may precipitate proteins because they denature them by reducing the RS—SR groups and precipitating these groups as —RSAg, for example.

The precipitation of proteins by cations is most pronounced on the basic side of the iso-electric point where the protein bears the greatest number of carboxylate anions. On the other hand, the precipitation of proteins with anions, such as picrate or phosphotungstate, takes place on the acid side of the iso-electric point where the cation groups of the protein are most abundant. This does not mean that the —NH_3^+ and —COO^- ions of the protein are the sole factors responsible for the precipitation of proteins but only that the effects of these ions are apt to be the determining factors in the precipitation reactions. It has been found, for example, that all of the copper which is combined with the proteins of milk can be liberated in strongly acid solutions two or three pH units less than the iso-electric point of the proteins.

Calcium and other alkaline earth ions form complexes with proteins. The complex formed by calcium with the blood plasma proteins has been repeatedly investigated. This complex is soluble and easily dissociated, and the difficulties in establishing its structure arise from the fact that there is no simple way to measure the activity of calcium ions in solution.

The uptake of most reagents by proteins is dependent upon so many factors that the behavior can frequently be best expressed as a sorption isotherm. Such a curve is a consequence of the activity of many different groups, but one should not be content to stop there and say that sorption accounts for the results. Each ion or molecule which is sorbed is held by one or two specific groups of atoms and it should be possible to obtain further knowledge about those groups by appropriate experiment.

Many globular proteins are insoluble in water at their iso-electric point. Others are soluble but are more easily precipitated by neutral agents such as alcohol or ammonium sulfate. Various reasons have been advanced to account for the minimum solubility at the iso-electric point. At this pH the number of positive and negative attached ions is equal and the precipitate could form without carrying down any counter-ions. It seems very probable that inter-ionic attractive forces are effective in holding the molecules of the precipitate together. The inter-ionic forces between ammonium and acetate ions in water are not as strong as the thermal disruptive energy, and therefore ammonium acetate is ionized in water. If, however, many $—NH_3^+$ and COO^- ions are bound together in single molecule the attractive forces will add up; but a large molecule will have no more thermal energy than one small ion. It thus seems probable that the globular proteins are held together, in part at least, by salt linkages when they are rendered insoluble by neutral agents.

A few proteins have been crystallized. With such large molecules, crystallization is a very slow process because each molecule must fit into its place with just the right alignment. In crystalline proteins not only salt linkages but also hydrogen bonds and van der Waals' forces must be effective in holding the crystal together. If the model shown in Figure 9–3 is correct, the egg albumin molecule exposes ionic groups only on its ends (and perhaps in a belt around the middle), whereas the sides present large surfaces of non-polar groups and peptide chains.

The solubility of proteins is reduced by any substance which reduces the activity of water in the solution. Concentrated salt solutions lower the solubility of proteins because water is attracted to the ions, leaving less water to dissolve the protein. Ions which take up large quantities of water of hydration will be more effective precipitating agents. Many proteins, however, require such a large quantity of salt in solution that only very soluble salts are effective. Ammonium sulfate has been used more than any other salt to precipitate proteins. Water-soluble non-electrolytes, such as alcohol, acetone and urea, precipitate proteins but usually denature them at room temperatures. At low temperatures denaturation is less serious.

The proteins which dissolve in water are soluble because they possess groups which have a strong affinity for water. Ions have a far greater affinity for water than any other groups, as was pointed out in Chapter 3, and it is the ionic groups on the protein molecule which give it its water solubility. Ionic groups, however, also have attractive forces for ions of the opposite charge and these attractive forces may lead to a lower solubility at the iso-electric point than on either side where there is an excess of ions of one charge. Any factor which increases inter-ionic attraction would be expected to lower the solubility. The partial replacement of water by a liquid of lower dielectric constant, such as alcohol, increases the inter-ionic attractive forces and lowers the solubility. Loss of solvent water by competition with added ions also produces the same result.

The early methods for separating proteins were based on the differing solubilities in salt solutions. In particular, serum globulins were precipitated by half saturated ammonium sulfate and albumin by the saturated salt. The separations achieved in this way were not quantitative and both fractions were contaminated. To obtain pure proteins, it is necessary to dissolve and reprecipitate the protein many times. One criterion for the purity of protein preparations is the solubility, which should be independent of the mass of the undissolved material. It must be admitted that very few proteins have been obtained in this state of purity.

Proteins, which have been precipitated by salts, come down as a flocculant precipitate which can best be described as "messy." They contain a large quantity of mother liquor including, of course, the salt used for precipitation. Filtration is not ordinarily practical but the precipitate may be collected by centrifugation. The salts can be removed from the resultant semisolid mass by dialysis. The precipitate is placed in a Visking sack and dialysed against water, preferably at low temperatures. During dialysis water moves into the sack by osmosis because of the high, although transient, osmotic pressure of the salts. Allowance for this increase in volume must be made when the sack is tied off. The water, which dilutes the protein in the sack at the end of dialysis, can most conveniently be removed by "pervaporation" which is a sort of dialysis against air. Pervaporation is carried out by hanging the sack of protein in a current of air. Water evaporates continuously from the surface leaving the protein in the sack.

A more recently developed method for the fractionation of proteins makes use of solvents such as alcohol or acetone at temperatures below 0° C.[4] At higher temperatures alcohol and other water soluble organic compounds precipitate proteins but they also denature them. By working at about $-5°$ C. it is possible to avoid denaturation and also reduce the danger of bacterial infection and enzymatic degradation of the protein. The solvents used as precipitants can then be conveniently removed by freezing the precipitated protein and evaporating off the ice and solvent at low pressure.

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[4] E. J. Cohn *et al.*, *J. Am. Chem. Soc.* **68**, 459–475 (1946).

The method of drying by freezing and evaporation from the frozen state is sometimes called lyophile drying. Colloids which have been "lyophilized" contain a network of fine pores which were occupied by the crystals of frozen solvent. This porous structure facilitates the re-solution of the colloidal substance when solvent is again added.

Large quantities of serum and serum proteins were lyophile dried for use on battle fronts in the recent war. The dried proteins will keep almost indefinitely and can be reconstituted in a matter of minutes by adding sterile distilled water. When colloidal materials are dried in air, the surface frequently dries out and hardens first, because the molecules are free to move and form a compact structure. This produces a skin or case-hardened layer which reduces the rate of further evaporation and makes re-solution extremely difficult.

The method of lyophile drying is applicable not only to aqueous solutions but has also been used for organic high polymers such as polystyrene and cellulose derivatives. These high polymers are especially difficult to dissolve because of the length, and consequent slow rate of diffusion, of the molecules. It may take weeks to dissolve a lump of solid polymer if the solution is not stirred continuously. A relatively dilute solution can be frozen and dried, leaving a highly porous structure. Upon addition of solvent, the material goes into solution immediately. The lyophile method is also of value in the determination of the weight of material in solution by drying to constant weight, since the porous structure increases the rate of drying by as much as a million fold over the rate of evaporation of a solvent from a solid nonporous mass.

Proteins, from their complex nature, might be expected to sorb a large variety of substances and such is indeed the case. Dry proteins, which may contain sorbed water, will sorb gases including HCl and NH_3 without any evidence of chemical reaction. Many organic solvent vapors are also sorbed. Some proteins, classified as gliadins or prolamines, are insoluble in aqueous systems but are soluble in 70% to 90% alcohol. These proteins contain a high proportion of non-polar side chains on the polypeptide chain. Alcohol can dissolve these chains and bring the protein into solution. The gliadins form fairly viscous solutions and are elongated rather than globular.

Some surface-active agents are strongly sorbed by proteins in solution. Anionic detergents (see page 214) are taken up by proteins on the basic side of the iso-electric point so the interaction is probably not a simple salt formation. Some sulfonated detergents denature proteins such as albumin to form viscous solutions in which the protein molecules are present as extended chains. The mixture can be extruded into a coagulating bath to make silk-like fibers as has been described on page 184. The nature of the interaction between protein and detergent appears to depend on both polar and non-polar attractive forces.

Electrokinetic Phenomena.—Ions are atoms or groups of atoms which bear an electric charge. Ions, in common with other charged objects, are attracted to any object bearing the opposite charge. Figure 9–5 shows two electrical conductors immersed in a solution and connected to a battery. The battery withdraws electrons from the positive electrode, which is called the anode, and supplies extra electrons to the negative electrode, which is called the cathode. If there were no ions in the solution between the electrodes, current would flow just long enough to charge the condenser consisting of the two electrodes.

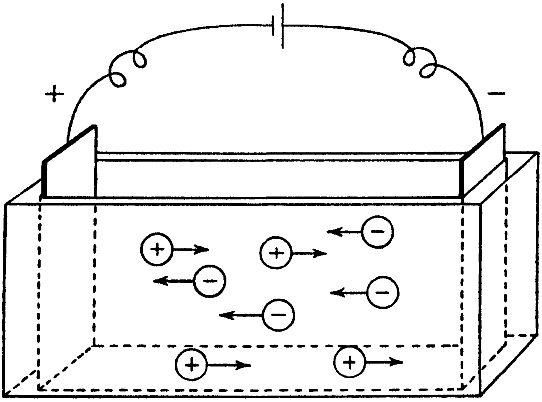


FIG. 9–5. Electrolysis cell.

When ions are present in the solution the positive cations will be attracted to the cathode and negative anions will be attracted to the anode. The attractive force on any ion is proportional to its charge. A divalent ion, such as Mg^{++}, is attracted with twice the force that attracts a monovalent ion, such as Na^{+}. The attractive force is also proportional to the potential gradient. In the apparatus shown in Figure 9–5 the potential gradient, E/l, is the difference in potential between the electrodes, E, divided by the distance between them, l.

It is necessary to specify both the applied voltage and the distance between the electrodes. If the electrodes are not parallel or do not fill the ends of the container the potential gradient will vary from point to point and is no longer equal to E/l.

An ion moves in an electric field at a velocity which produces a viscous drag on the ion exactly equal to the force of electrical attraction. The velocity of an ion in an electric field of 1 volt per cm is called its mobility, v. The observed velocity, V, is therefore equal to the mobility times the potential gradient.

$$V = vE/l.$$

In the case of simple ions it is usual to calculate an equivalent mobility, λ, such that

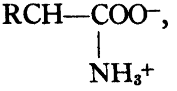
$$v = \lambda z/F \qquad (9\text{–}2)$$

where z is the valence of the ion and F is Faraday's constant. The equivalent mobility is directly related to the force necessary to move an ion and can be related to the size of large ions by Stokes' law,

$$\lambda = F/6\pi\eta r = F/3\pi\eta d. \qquad (9\text{–}3)$$

Stokes' law does not, however, apply to small ions comparable in size with water molecules. The diffusion coefficient, D, if corrected for the effects of other ions, can also be related to the equivalent mobility of an ion by the equation,

$$\lambda = FD/kT \qquad (9\text{–}4)$$

where k is Boltzmann's constant and T is the absolute temperature. The charge on an ion can theoretically be calculated from equations 9–2 and 9–3 above. Equations 9–2 and 9–4 can be used to calculate the charge if the diffusion coefficient is known. It is therefore possible to estimate the net number of charges on a particle by comparing the electrical mobility with the equivalent mobility calculated from the diffusion coefficient. These measurements give no indication of the total number of charges on a particle since the observed velocity is a result of the net force acting on the ions. A zwitter-ion, such as a simple amino acid  $\underset{NH_3^+}{\underset{|}{RCH}}\text{—}COO^-$, would be attracted with equal force in opposite directions and would not move in an electric field; nor would it conduct an electric current.

So far attention has been centered on the behavior of ions in the body of the solution. At the electrodes some reaction must take place in order that a current may flow. The chemical reaction may have nothing to do with the ions which carry the current in the solution. If, for example, Na_2SO_4 is dissolved in water and platinum electrodes are inserted and attached to a battery

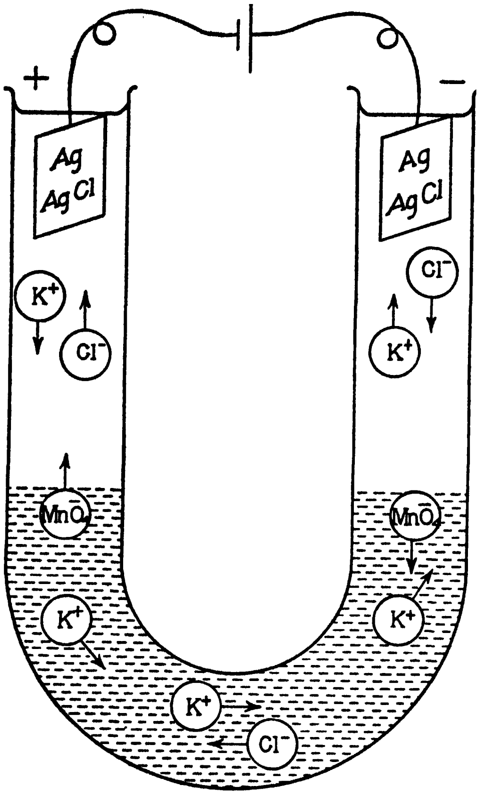


FIG. 9–6. A U-Tube electrolysis cell containing $KMnO_4$ overlaid by KCl.

the Na^+ and $SO_4^{=}$ ions will carry the current in the solution. Neither of these ions will react at the electrodes, however, and the following electronic reactions will take place:

$$\text{At the anode } 4\,H_2O + 4\,e^- \longrightarrow 4\,OH^- + 2\,H_2.$$

$$\text{At the cathode } 4\,H_2O \longrightarrow 4\,H^+ + O_2 + 4\,e^-.$$

Gas will be liberated at both electrodes which might be troublesome if one wanted to keep the volume constant. A better electrode arrangement involves the use of silver wires covered with silver chloride in a solution of any chloride. The electrode reactions here are:

$$\text{anode } AgCl + e^- \longrightarrow Ag + Cl^-$$

$$\text{cathode } Ag + Cl^- \longrightarrow AgCl + e^-$$

and as long as the anode remains covered with AgCl no gas will be liberated. Copper in copper sulfate is also used as a non-gassing electrode.

The movement of an ion in solution can be followed if it happens to be colored. A solution of potassium permanganate and potassium chloride could be placed under solutions of potassium chloride in the apparatus shown in Figure 9–6. If a potential of 100 volts is applied and the average distance between the electrodes is 10 cm the voltage gradient E/l will be 10 volts per cm, assuming that all the solutions have the same conductivity. The MnO_4^- ion will move up in the anode chamber and down in the cathode chamber. The equivalent mobility, λ, of the MnO_4^- ion is about 62 at 25° C. The velocity of the MnO_4^- ion under the conditions stated will therefore be

$$V = (\lambda z/F)\,(E/l) = (62 \times 1/96{,}500)\,(100/10) = 0.0064 \text{ cm/sec.} \tag{9–5}$$

The boundary between the MnO_4^- ion and the clear solution will move 0.0064 cm in 1 second or about 4 cm in 10 minutes.

The movement of colorless ions in solution can be followed by observing the changes in refractive index which are produced by the dissolved substance. A beam of light is bent when it passes through a region where the refractive index is changing, just as it is bent when it passes through a prism. By suitable optical means it is possible to represent the steepness of the gradient as a displacement and make a photograph of the boundaries caused by substances of varying mobilities.

We are indebted to Tiselius, one of the workers in Svedberg's laboratory, for the development of the modern apparatus for the measurement of the mobilities of proteins in solution. Tiselius modified the conventional U tube so that one section could be slid over another. In this way he was able to get sharp initial boundaries. The U tube in a Tiselius moving boundary apparatus is made of pieces of plate glass so that the position of the boundary can be observed accurately. When a mixture of proteins in a buffer solution is placed in the lower half of the U tube and overlaid with pure buffer, each protein will migrate with its characteristic mobility. The protein with the greatest mobility will move farthest up one arm of the U tube. Below the first protein boundary will be boundaries of the other proteins in the order of their mobilities.

Figure 9–7a shows a mixture of three different proteins in the U tube before the parts are slid together. Figure 9–7b shows the separation produced when the current has flowed for a period. Each kind of protein is represented by a different symbol. The open circles represent the slowest molecules and the solid black circles represent the fastest molecules. Figure 9–7c shows how the separation can be improved by forcing liquid back through the U tube as indicated by the arrows. This figure shows an ideal case; it would be possible to separate the U tube at this point and recover pure samples of proteins p and p''.

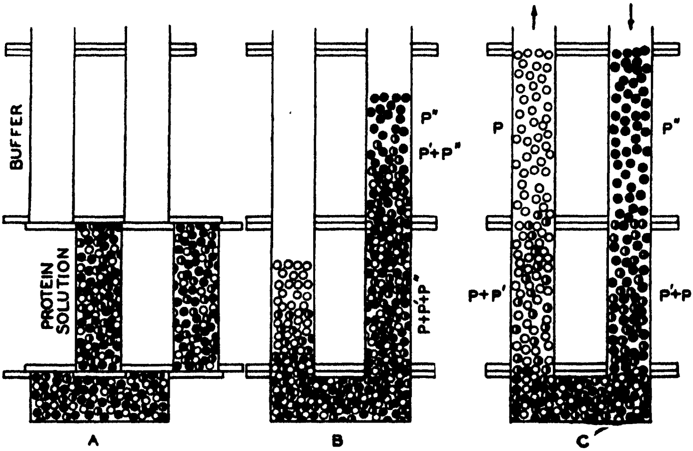
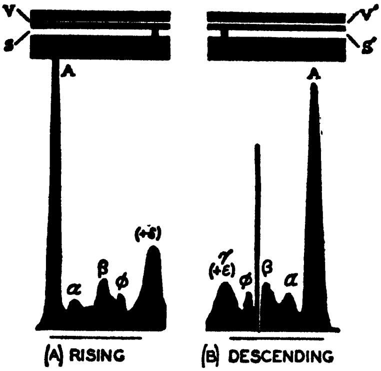


Fig. 9–7. Diagram showing the movement of three components of a mixture during electrolysis in a Tiselius U-tube. In part c the fluid has been displaced in the direction of the arrows. (From Abramson, Moyer and Gorin, *Electrophoresis of Proteins*, Reinhold (1942).)

An optical examination of the refractive indices in Figure 9–7b would show the following boundaries. Near the top of the right leg of the U tube would be a boundary between the buffer and protein p'', lower down would be a boundary between p'' and $p' + p''$, and below it would be a boundary between $p' + p''$ and the mixture of all three proteins. In the left leg the situation would be the reverse. There are several techniques which permit one to portray these boundaries. One of the most successful has been developed by Longsworth[5] and a pattern of the boundaries produced by human plasma is shown in Figure 9–8. In this figure the horizontal axis represents the vertical axis of the U tube. The vertical axis of the figure represents the steepness of the gradient of refractive index which is proportional to the gradient of concentration. The proteins which are present in human serum are each represented by a peak on the diagram. The area of any peak is directly proportional to the concentration of the protein which produces it. "A" represents the albumin and the Greek letters represent various globulin fractions.

[5] See references at the end of this chapter.

Mobility patterns obtained with the Tiselius apparatus are always presented in differential form. The height of any part of the curve is proportional to dc/dx, the differential of the concentration with distance up or down the tube. The total concentration of proteins at any point in the U tube could be obtained by integrating the differential mobility pattern if there were any reason for doing so.



(A) RISING (B) DESCENDING

Fig. 9–8. Electrophoresis pattern of normal human plasma using the Longsworth scanning technique. (From Abramson, Moyer and Gorin, *Electrophoresis of Proteins*, Reinhold (1942).)

Electrophoresis.—The movement of colloidal particles in an electrical field is called electrophoresis, or sometimes cataphoresis. Electrophoresis of colloidal particles is the same effect that we call ionic mobility when we deal with small ions consisting of one or a few atoms. It has been customary, in the case of small ions, to report ionic mobility measurements in terms of the equivalent mobility, λ, which equals vF/z. In some cases λ is calculated from observations of v, in others λ is derived from conductivity and transference measurements.

The net number of charges on a colloidal particle, z, cannot be readily determined and it has been customary in the past to convert colloidal mobilities into another derived parameter the zeta potential, ζ. The zeta potential is defined by the equation,

$$\zeta = v\,4\pi\eta/K \tag{9–6}$$

where η is the viscosity and K the dielectric constant.

The zeta potential has been extensively used in colloidal chemistry and its use has frequently introduced much confusion. Helmholtz derived the equation which defines the zeta potential from the rate of movement of a conducting sphere, charged to the potential zeta, and moving between electrodes in a medium having a viscosity, η, and a dielectric constant, K. We do not know with any accuracy the dielectric constant of water close to an ion; it is certainly much less than the value in pure water which is ordinarily employed in calculations of the zeta potential. There is also some doubt regarding the viscosity of the fluid close to a particle. The correct value probably lies between the viscosity of the solution and the viscosity of the pure solvent. The value for the pure solvent has ordinarily been used in calculations. In many respects the zeta potential is an unsatisfactory derived value. For precision work it is always preferable to report data in terms of measured mobilities (as well as in terms of zeta potentials if desired). The factor by which zeta potentials must be multiplied to re-convert them to mobilities is 2.48×10^{-3} at 18° C. and 1.44×10^{-3} at 25° C. A zeta potential of 100 millivolts (0.1 volt) corresponds to a mobility of 1.44×10^{-4} cm per sec or 1.44 microns per second at 25° C.

It can be shown that the zeta potential and the mobility of a particle are both directly related to the charge density on the surface. A particle bearing no net charge will have a zero mobility and zero zeta potential. Furthermore, in a given medium, the velocity of a particle will depend upon the net number of ions on its surface and on the size of the particle.

The mobility and the zeta potential of large particles are both reduced by the presence of other ions in solution. When a particle moves through a solution it carries with it a part of the solution which surrounds it. Molecules of solvent which are very close to the particle will move almost as fast as the particle, and molecules farther out will move more slowly than the particle but in the same direction. The average result is the same as if the particle carried with it a shell of liquid, with one important difference. The molecules which make up the liquid shell are continuously changing as some are left behind and new ones are picked up in front.

If other ions, present in the solution, happen to be inside the shell of liquid which moves with the particle they will, of course, be dragged along too and the effective charge on the particle will include the ions that accompany it when it moves. In the neighborhood of a particle bearing positive ionic groups there will be more negative than positive ions. In very dilute solutions these negative counter-ions will be far away from the particle and only occasionally will there be one in the liquid shell which moves with the particle. Figure 9–9a shows a particle surrounded by a shell of liquid which moves with the particle. The counter-ions are present in dilute solution and in this case only one counter-ion is present inside the shell.

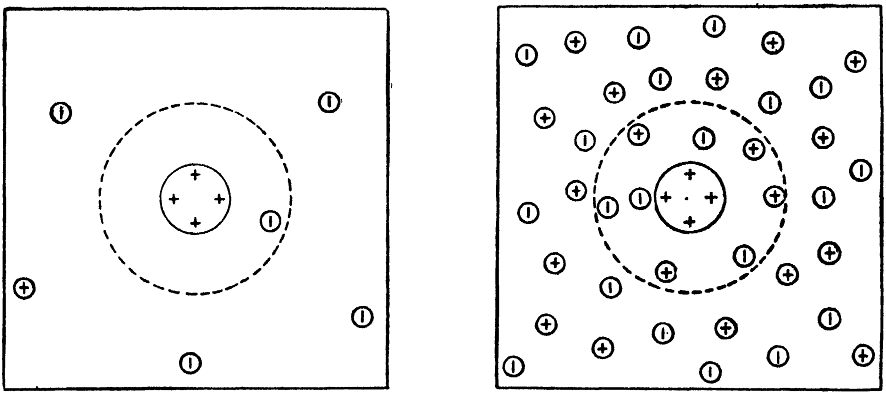


FIG. 9–9. Schematic representation of the ionic atmosphere around a small ionized particle.

Figure 9–9b shows the same particle in a concentrated solution and here there are three counter-ions and two other pair of ions present in the shell that moves with the particle. The more concentrated the solution the more ions will be present in the shell and the lower will be effective charge on the particle. This reduces its mobility and we can say in general that the mobility and the zeta potential of ionized particles are reduced by the presence of other ions in the solution.

The effect of other ions in solution is proportional, as a first approximation, to the square root of the ionic strength. The ionic strength for any given salt is proportional to the concentration, but polyvalent ions have a larger proportionality factor than monovalent ions. The ionic strength, μ, may be defined as one half the sum of the molar concentrations of each ion, times the square of its valence.

$$\mu = 1/2\Sigma cz^2. \tag{9-7}$$

For NaCl and similar salts $\mu = c$; for $CaCl_2$ or Na_2SO_4 $\mu = 3c$; for $MgSO_4$ $\mu = 4c$; and for $LaCl_3$ $\mu = 6c$.

The effect of polyvalent ions on most colloidal systems is very much greater than would be expected on the basis of their valence. Furthermore, these effects are exerted only by polyvalent ions of opposite charge to the ionic groups on the colloid. In many if not most cases these effects are the result of the polyvalent ion combining with the colloidal particle. For example, an Al^{+++} ion might combine with $—COO^-$ groups of a protein molecule forming

—$COOAl^{++}$. This combination could occur when the Al^{+++} ions were too dilute to produce an appreciable concentration of these ions inside the shell of water that moves with the protein molecule. By combining with the particles, Al^{+++} ions have an effect on the ionic mobilities at much lower concentrations than would have been predicted from the ionic strength of the solution.

Electroosmosis.—When particles bearing ionized groups are placed in an electric field they move toward the electrode of opposite charge. If we now look at the counter-ions, which are present in the solution to balance the charges on the colloidal particles, we see that they are moving in the opposite direction to the particles and that they drag with them shells of water just as the larger particles do. Now if we attach the colloidal particles to a framework (for instance, we might stick them on a membrane, and then put the membrane in an electric field), the counter-ions will still move and they will drag water through the membrane. The movement of solution through a membrane under the influence of an electrical current is called electroosmosis. Electroosmosis, sometimes called electroendosmosis, can be produced by placing any membrane which bears ionic groups in an electrical field. Figure 9–10 shows a possible arrangement. A

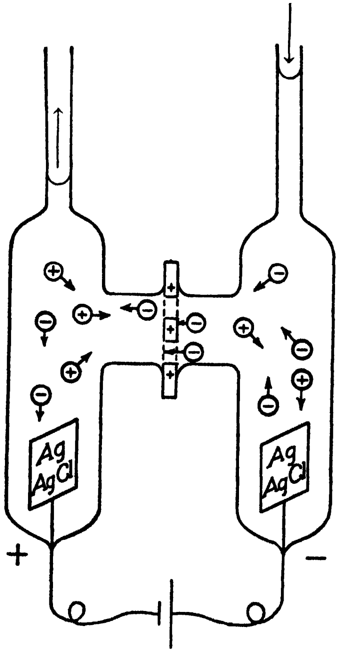


FIG. 9–10. Electro-osmosis through an ionized membrane.

membrane bearing negative ions, such as —COO^-, on its surface is placed between the two electrodes. The solution will rise in the cathode compartment because the positive counter-ions carry water with them as they move toward the cathode.

Most capillary systems are large compared with the distances between ions and the counter-ions are concentrated along the walls of the capillaries. These counter-ions will move along the surface of the capillary and will pull with them all of the fluid in the capillary. This prediction is experimentally verified by the fact that the linear velocity of movement of solution through a capillary is independent of the size of the capillary and depends only on the charge-density on its walls and on the concentration of ions in the solution. The linear velocity of the solution in the capillary, v, can be calculated as a zeta potential by the same equation relating the electrophoretic mobility to the zeta potential,

$$\zeta = v\,4\pi\eta/K. \tag{9-8}$$

In many capillary systems which occur in membranes it is not possible to measure the linear velocity of the water through the pores, but the bulk flow, V, in cubic centimeters per second can be measured. In this case it can be shown that

$$v = VI/L \qquad \text{and} \qquad \zeta = V\,4\pi\eta L/ID \tag{9-9}$$

where L is the conductivity of the solution and I is the current flow. The conductivity should be measured inside the capillaries but is ordinarily measured on the bulk solution. In small capillaries with highly charged walls which contain dilute solutions this can lead to large errors because there will be more ions in the pores than in the solution and the conductivity in the pores will be greater than that in the solution.

Water-soluble proteins are sorbed on nearly all surfaces and produce a charge-density on the surfaces which is the same as the charge-density on the protein molecules themselves. As a result the electrophoretic mobility of any particle which is covered with sorbed protein will be the same as the mobility of the protein molecules.

The measurement of the electrophoretic mobility of a protein molecule is difficult, but the measurement of the electrophoretic mobility of a quartz particle covered with the sorbed protein can be quite easy under a microscope. In any measurement of electrophoresis it is necessary to correct for the fact that the solution is also moving along the walls in the opposite direction by electroosmosis. In a closed cell this produces a return flow down the center. In a thin flat cell the fluid motion is shown in Figure 9–11. It will be seen that there is no fluid motion at levels which are 21% of the total height of cell above the bottom or below the top of the cell. If electrophoresis is observed at these levels there will be no correction for electroosmotic flow. Figure 9–12 is a diagram of a flat electrophoresis cell designed for use on a microscopic stage. This cell is fitted with stopcocks for filling and has two glass struts to make the assembly more rigid.

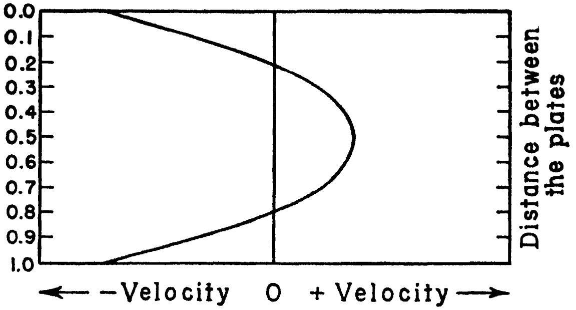


FIG. 9–11. The velocity of electro-osmotic flow between two flat plates in a closed system.

Not only is the electrophoretic mobility of protein molecules and sorbed proteins identical, but the electroosmotic mobility of a protein solution in a capillary coated with sorbed protein is identical with the electrophoretic mobility of particles covered with sorbed protein. What this really means is that electrophoresis and electroosmosis are two measurements of the same thing. In either case we measure the movement of a surface relative to a fluid. If the fluid does not move we measure the movement of the particles and call it electrophoresis; if the particles form a rigid structure which does not move we measure the movement of the fluid and call it electroosmosis.

Other Electrokinetic Phenomena.—When a potential difference is applied across a membrane which has attached ions on its pores, the solution will move through the pores by electroosmosis and will build up a pressure until the back flow through the center of the capillary exactly equals the flow along the walls. This pressure is built up in the electrophoresis cells described in the previous section. The magnitude of the pressure can be calculated for pores of known diameter. For any given diaphragm material the pressure is proportional to the mobility, v, and the applied potential.

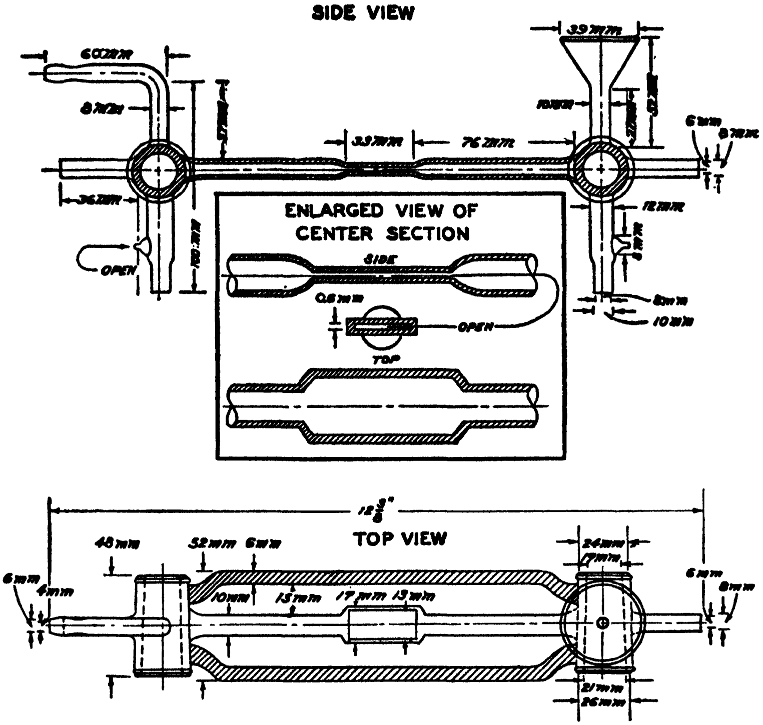


FIG. 9–12. Working drawing of the flat horizontal electrophoresis cell made of one piece of glass. (From Abramson, Moyer and Gorin, *Electrophoresis of Proteins*, Reinhold (1942).)

If a solution is forced through a membrane which has attached ions on its pores, one might expect a potential difference to be built up as the mobile counter-ions are pushed through the capillary and accumulate in one chamber. Such a potential actually is produced and is known as the streaming potential. The streaming potential is proportional to the applied pressure and to the mobility, v, of the solution in the pores of the membrane.

$$E = vP/L \tag{9–10}$$

where E is the streaming potential and P is the applied pressure. Electrophoresis is the movement of ionized particles in an electrical field and there is, as you might expect, a parallel phenomenon which is called the sedimentation potential. The sedimentation potential is the potential produced by the sedimentation of ionized particles in a gravitational or centrifugal field. It is not easy to make accurate measurements of the sedimentation potential and the equations relating it to the electrophoretic mobility of the particles will not be presented.

The magnitude of all electrokinetic phenomena, electrophoresis, electroosmosis, streaming potential and sedimentation potential is directly proportional to the mobility of the solid material relative to the liquid. The mobility in turn depends upon the density of ionic groups on the surface and the concentration of ions in solution. Increased concentration of ions in solution always reduces the magnitude of electrokinetic phenomena with only occasional exceptions in the case of some polyvalent ions.

Combination of one trivalent cation such as Al^{+++} with every monovalent anion such as COO^- on the surface of a particle to form $COOAl^{++}$ would reverse the sign of the charges on the particle and double their number.

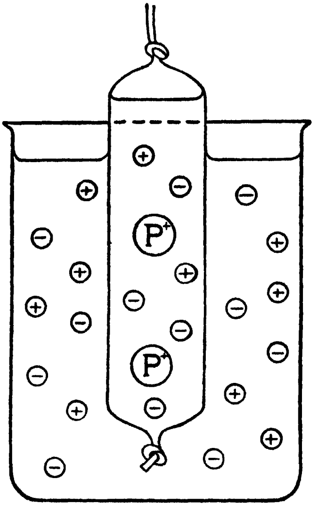


FIG. 9–13. A system representing the Donnan equilibrium. The Visking sack is permeable to the small ions but not to the large P^+ ions.

The Donnan Equilibrium.—The Donnan equilibrium, which is sometimes called the Gibbs-Donnan equilibrium in honor of Willard Gibbs who predicted it and F. G. Donnan who investigated it, is the equilibrium condition which exists in a system containing at least one ion which cannot diffuse. The simplest example of a Donnan equilibrium is furnished by the system shown in Figure 9–13. The vessel contains a membrane which has pores large enough to permit small ions such as Na^+ and Cl^- to penetrate, but large ions, such as protein ions bearing a net positive charge, cannot get through the pores. The following conditions must be satisfied by a system of this sort.

1. Each side must contain equal numbers of cations and anions, for electroneutrality must be preserved. We will let (Na^+) represent the concentration of the sodium ions inside the membrane and $(Na^+)_0$ represent their concentration outside the membrane. Likewise (Cl^-) and $(Cl^-)_0$ represent the chloride ion concentrations inside and outside and (Pr^+) represents the protein ion concentration inside. Our first condition can then be stated:

$$(Na^+) + (Pr^+) = (Cl^-) \text{ for the inside solution} \qquad (9\text{–}11)$$

and

$$(Na^+)_0 = (Cl^-)_0 \text{ for the outside solution.} \qquad (9\text{–}12)$$

2. At equilibrium the product of the concentrations of any diffusible ion pair must be equal on the two sides of the membrane,

$$(Na^+)\ (Cl^-) = (Na^+)_0\ (Cl^-)_0. \qquad (9\text{–}13)$$

This second condition may not be so obvious. Consider, however, a system that is saturated with NaCl. In any saturated solution the solubility product, which is the product of the concentrations of the ions which form the salt, will be equal to a constant. Now, since the system is at equilibrium, the solution inside the membrane must be saturated if the solution outside is saturated, and the solubility products will be the same on both sides of the membrane. This is our second condition. It can be shown by more advanced methods that equation 9–13 holds when the salt is not saturated on both sides of the membrane.

Students who have had physical chemistry will recognize that equation 9–13 should be written in terms of ionic activities rather than concentrations. Over the range of concentrations covered by most practical examples of the Donnan equilibrium, equation 9–13 expresses the facts with reasonable accuracy. The inclusion of the activity coefficients unnecessarily complicates the subsequent mathematical treatment.

Our first condition for equilibrium tells us that there will be fewer Na^+ ions than Cl^- ions inside the membrane because there must be one Cl^- ion for each positive ion and there are Pr^+ ions as well as Na^+ ions inside the membrane. Equations 9–11, 9–12 and 9–13 can readily be solved for the concentration of any ion in terms of the concentrations of any two of the others. It will be instructive to consider a few idealized examples. Let us specify the concentrations (Na^+) and (Pr^+) inside the membrane and see what the concentration of the outside solutions will be.

First let us see what happens when the concentrations (Na^+) and (Pr^+) are equal to each other. Let us say that each equals one unit. Then the (Cl^-) concentration must be 1 + 1 or 2 by equation 9–11. The ion product is therefore 1 times 2 or 2, both inside and outside. Since the concentrations of $(Na^+)_0$ and $(Cl^-)_0$ are equal, we know that $(Na^+)_0^2 = 2$. Therefore $(Na^+)_0$ equals $\sqrt{2}$ or 1.41 which is also the value of $(Cl^-)_0$.

The results of the equilibrium represented by this example are shown in the third line of Table 9–2, which also includes the results of the other cases which follow.

Let us now consider what happens when the concentration of (Pr^+) is greater than (Na^+) on the inside. Let (Pr^+) equal 1.0 and (Na^+) equal 0.1. Then (Cl^-) will equal 1.1 and the ion product will be 0.11. Therefore the concentration of either outside ion $(Na^+)_0$ or $(Cl^-)_0$ is the square root of 0.11 which is 0.33. This is shown as the second line of Table 9–2.

When we go in the opposite direction and let the concentration of (Na^+) exceed that of (Pr^+) we get results such as are shown in the fourth line of Table 9–2. We let (Pr^+) equal 1 as before and let (Na^+) equal 10. (Cl^-) will equal 11 and the ion product will be 110. The concentration of either outside ion will be $\sqrt{110}$ or 10.49.

The final extreme case would be an infinite concentration of salt. This is not realizable but we can consider what happens when (Pr^+) is zero and (Na^+) is 1. (Cl^-) will also be 1 and so will $(Na^+)_0$ and $(Cl^-)_0$. This extreme, trivial as it may be, is included for completeness as the fifth line of Table 9–2.

From the cases presented in Table 9–2 you can see that the Donnan equilibrium produces deviations from equal concentrations of all diffusible ions only when the concentration of the nondiffusible ion is comparable with or larger than the concentration of the diffusible electrolytes. When (Pr^+) is small it has very little effect on the concentrations of (Na^+) and (Cl^-). Obviously the same considerations will apply to a colloidal ion bearing a negative charge. Other diffusible ions can of course be substituted for (Na^+) and (Cl^-).

When a mixture of diffusible ions is present in a system containing a colloid, equations 9–11 and 9–12 apply to the sum of all the cations and the sum of all the anions. An equation similar to 9–13

TABLE 9–2. EXAMPLES OF THE DONNAN EQUILIBRIUM FOR A SYSTEM CONTAINING Na^+, Cl^- AND Pr^+ INSIDE A MEMBRANE AND Na^+ AND Cl^- OUTSIDE THE MEMBRANE

Case	Inside Concentrations				Outside Concentrations		Ionic Ratio	Osmotic Difference
	(Pr^+)	(Na^+)	(Cl^-)	$(Na + Cl)$	$(Na^+)_0$	$(Na + Cl)_0$	$(Na^+)/(Na^+)_0$	$(Na + Cl) - (Na + Cl)_0$
I	1.0	0.0	1.0	1.0	0.0	0.0	0.0	1.0
II	1.0	0.1	1.1	1.2	0.33	0.66	0.302	0.54
III	1.0	1.0	2.0	3.0	1.41	2.82	0.707	0.18
IV	1.0	10.0	11.0	21.0	10.49	20.98	0.954	0.02
V	0.0	1.0	1.0	2.0	1.0	2.0	1.0	0.0

can be set up for every pair of diffusible ions of opposite charge. It can also be shown that the ratio of the concentrations of any cation outside to inside, $(M^+)_0/(M^+)$ is equal to the inverse ratio of the concentration of any anion inside to outside $(A^-)/(A^-)_0$.

From equations 9–11, 9–12 and 9–13, we get

$$(Na^+)\cdot[(Na^+) + (Pr^+)] = (Na^+)_0\cdot(Cl^-)_0 = (Na^+)_0^2.$$

Solving for $(Na^+)_0$, we find that

$$(Na^+)_0 = \sqrt{(Na^+)\cdot[(Na^+) + Pr^+)]}$$

and the ratio

$$\frac{(Na^+)_0}{(Na^+)} = \frac{\sqrt{(Na^+)\cdot[(Na^+) + (Pr^+)]}}{(Na^+)} = \sqrt{\frac{(Na^+) + (Pr^+)}{(Na^+)}}.$$

Likewise, since $(Cl^-)_0 = (Na^+)_0$,

$$(Cl^-)_0 = \sqrt{(Na^+)\cdot[(Na^+) + (Pr^+)]}$$

and

$$\frac{(Cl^-)}{(Cl^-)_0} = \frac{(Na^+) + (Pr^+)}{\sqrt{(Na^+)\cdot[(Na^+) + (Pr^+)]}} = \sqrt{\frac{(Na^+) + (Pr^+)}{(Na^+)}}.$$

We can say in general that for any cation the ratio of the concentrations $(M^+)_0/(M^+)$ is constant and equal to the inverse ratio for any anion, $(A^-)/(A^-)_0$.

If a pair of electrodes reversible to chloride ions were placed one inside and one outside of the membrane, no current could flow because the system is in equilibrium. Nevertheless, the potential at the inside electrode would be

$$E = E_s + (RT/F) \ln (Cl^-) \qquad (9\text{–}14)$$

and the potential at the outside electrode would be

$$E_0 = E_s + (RT/F) \ln (Cl^-)_0. \qquad (9\text{–}15)$$

The difference in the potentials between the two electrodes would be

$$E - E_0 = (RT/F) \ln [(Cl^-)/(Cl^-)_0]. \qquad (9\text{–}16)$$

The value of $(Cl^-)/(Cl^-)_0$ is not unity and its logarithm is not zero if there is a nondiffusible ion, Pr^+, in the system. Therefore, there must be another potential in the system which exactly balances the potential difference between the electrodes. This potential is called the Donnan membrane potential. It cannot be measured by reversible electrodes such as Ag—AgCl or by glass electrodes.

If the membrane were by-passed by a salt bridge we could measure the potential between the two reversible electrodes in solutions which have different chloride ion concentrations. More conveniently we could use salt bridges on the two electrodes so that they no longer respond to the (Cl^-) concentration. By the use of salt bridges connected to nonpolarizable electrodes, such as calomel electrodes, it is possible to measure the membrane potential directly. Figure 9–14 shows the various potentials which exist in a system in Donnan equilibrium. It must be emphasized that *no current can be drawn from a system in equilibrium.* The potential observed between the calomel electrodes exists only because the salt bridges represent a non-equilibrium condition. This almost eliminates the effect of the concentration of the various ions in the solution on the potential so long as K^+ and Cl^- ions are diffusing from the salt bridge into the solutions.

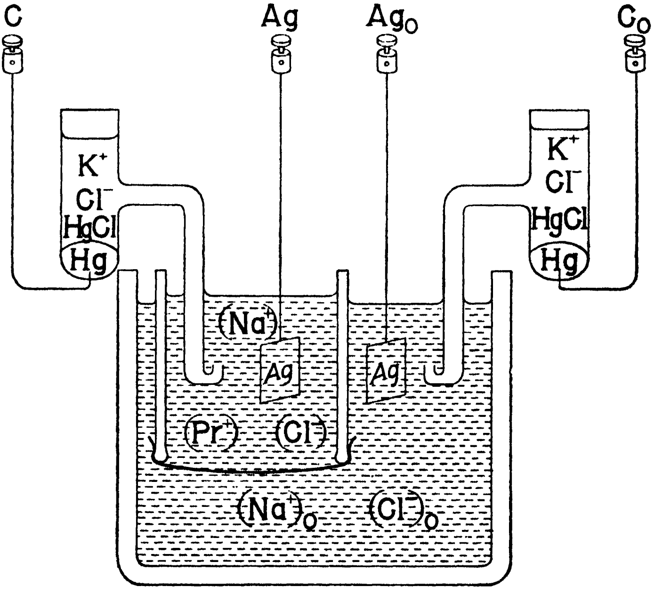


FIG. 9–14. Potentials in a system in Donnan equilibrium.

(a) Inside the membrane.

The Ag-Ag Cl electrode potential is $E = E_s + \frac{RT}{F} \ln(Cl)^-$

The calomel electrode potential is C = a constant (very nearly).

(b) Outside the membrane.

The Ag-AgCl electrode potential is $E_0 = E_s + \frac{RT}{F} \ln(Cl)_0^-$

The calomel electrode potential is $C_0 = C =$ a constant.

(c) The membrane potential is M.

(d) The potential between the reversible silver electrodes is zero.

$\Delta E = E - E_0 + M = O$. Therefore $M = E_0 - E = \frac{RT}{F} \ln \frac{(Cl^-)_0}{(Cl^-)}$

(e) The potential between calomel electrodes is M. $\Delta E = C - C_0 + M = M$.

The Donnan equilibrium produces osmotic effects as well as electrical effects. If you refer back to Table 9–2 you will find in the last column a tabulation of the difference between the total concentration of diffusible ions inside and outside the membrane. The concentration of $Na^+ + Cl^-$ inside is always greater than outside although the difference becomes small at high salt concentrations.

Osmotic pressure depends upon the total number of particles, including ions, in solution (see Chapter 2). The osmotic pressure difference across a membrane is proportional to the difference in the concentration of particles on the two sides. Now if we were to attempt to measure the osmotic pressure of a protein in solution we would find that the osmotic pressure was too high because it includes the osmotic pressure caused by the counter-ions inside the membrane. As we add salt to the system we reduce this effect, and reference to the last column of Table 9–2 shows that the error is only 2% of the equivalent concentration of the protein when the concentration of the external salt solution is about ten times the equivalent concentration of the protein solution.

It is also possible, with some protein solutions, to eliminate the osmotic error by working at the iso-electric point where the protein has no net charge. Many colloids are, however, not stable at their iso-electric points, and osmotic measurements can be made only if electrolytes are added to reduce the magnitude of the Donnan effect.

You will have noticed that both the Donnan equilibrium effects and electrokinetic effects are reduced by the presence of electrolytes. In electrolyte solutions as concentrated as those which are found in the body fluids, most electrokinetic and Donnan effects are reduced to very small values. Neither phenomenon can account for the relatively large bio-electric potentials which are produced by all living organisms. The outstanding example is, of course, the electric eel which can produce from its battery a potential of over 100 volts.

The Swelling of Ionic Gels.—In the derivation of the Donnan equilibrium it is necessary to postulate only that at least one ion is kept inside one part of the system. For convenience we set up a membrane impermeable to large ions but permeable to small ions. Any other effect which keeps one species of ions from diffusing freely will also produce a Donnan equilibrium. Ionic groups which are attached to the structure of a gel cannot diffuse out into the surrounding solution and accordingly gels should show a Donnan equilibrium.

When a dry protein gel (such as a cube of dry gelatine) is immersed in cold water it swells in the water up to a certain size and does not swell further. The swollen gel is turgid and resilient, rather like an inflated balloon. These properties suggest that the water in the gel is under pressure. The gel behaves as if its surface were a membrane restraining particles which produce an osmotic pressure. The swollen gelatin is analogous to a Visking sack full of a soluble protein which swells up, until the hydrostatic pressure inside the sack equals the osmotic pressure of the solution inside. In the case of the Visking sack, it is the pores of the membrane which restrain the protein molecules and their counter-ions. In the case of the gelatine cube it is the structure of the gel which restrains the ionic groups on the proteins and their counter-ions.

All of the molecular chains of a protein gel can be considered as tied together into one molecule. Nearly all of the osmotic effect will be due to the counter-ions. We should therefore expect the swelling of a protein gel to be minimal at the iso-electric point where there are no counter-ions. On either side of the iso-electric point, counter-ions will be present in the gel and will contribute to the osmotic swelling. A gel will obey the Donnan equilibrium and the osmotic excess will decrease as salts are added to the system. A gel which is not at its iso-electric point will, therefore, swell less in salt solutions than it does in pure water.

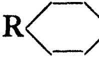
Even at their iso-electric points, gels do swell and non-ionic systems, such as vulcanized rubber in benzene, also swell. Swelling is obviously not due to the presence of counter-ions in the latter case and we must look elsewhere to find a mechanism for the swelling. Although a piece of vulcanized rubber may be considered to be one molecule, it consists of chains which are long enough between the cross linkages to be able to move about as independent kinetic units, as was shown in Chapter 7. In the presence of solvent, each kinetic unit will contribute to the osmotic pressure and will lower the activity of the solvent so that more solvent will enter the structure and cause swelling. Proteins at their isoelectric point also behave in a similar fashion.

In any gel, swelling takes place until the tension in the fibrils, or molecular chains of the gel structure, produces a pressure just equal to the swelling pressure. The extent of the swelling is dependent on the length of the chains between points of attachment, as well as on the number of attached ions. Gelatine, which is partially hydrolized collagen, consists of long molecular chains. When a solution of gelatine in warm water is cooled, secondary forces unite the chains to form a gel structure. Heating loosens these forces and the gel dissolves or "melts."

If we make two gels, each containing 1 gm of gelatine, the first in 20, and the second in 40 ml of water, and dry the gels, they will shrink down to about the same dry volume. When these dry gels are immersed in water the gel made with 40 ml of water will swell more than the gel made with 20 ml of water. Evidently the distance between cross links was greater in the more dilute gel and it recovered more of its original volume.

Colloidal Electrolytes.—Colloidal electrolytes are substances which form, in solution, ionized particles of colloidal dimensions. McBain and many others restrict the term colloidal electrolyte to those substances which dissociate to form simple noncolloidal ions in sufficiently dilute solutions, but which reversibly associate to form colloidal micelles, or clusters which contain ions of both signs, in more concentrated solutions. The term colloidal electrolyte is ordinarily not used for soluble proteins, nor for large ionized polymers such as the polyphosphate ions. These ions have many of the properties of colloidal electrolytes but do not reversibly ionize to small ions in dilute solution. Many of them are unstable and hydrolyze to smaller ions in dilute solutions but the ions do not associate again into large micelles when the solutions are concentrated.

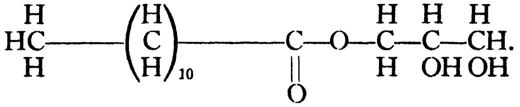
The common colloidal electrolytes include the soaps, organic detergents and the dyes. Soaps and other organic detergents and wetting agents consist of a hydrocarbon portion which contains from about eight up to about twenty carbon atoms and at least one ionizable group. These substances constitute one group of the more general class of surface-active agents discussed in Chapter 3. Dyes are not noted for their surface active properties, although some dyes do lower the surface tension of water and are positively sorbed on the air-water interface.

The colloidal electrolytes, which have soap-like properties, have a hydrocarbon portion and an anionic or a cationic group. The more common anionic groups include carboxylate, $RCOO^-$ (in the natural soaps); sulfate, $ROSO_3^-$; aliphatic sulfonate, RSO_3^-; aromatic sulfonate, RSO_3^-; and the phosphate esters, $ROPO_3^{=}$ and $RR'OPO_2^-$. The sulfate and sulfonate ions form strong acids which are almost completely ionized in dilute solution. The carboxylate ion is a weak acid and reverts to the un-ionized —COOH group in solutions less basic than pH 9. The more common cationic groups found on colloidal electrolytes include substituted ammonium, RNH_3^+; quaternary ammonium, NR_4^+; pyridinium, $C_6H_5NR^+$; quaternary phosphonium, PR_4^+; and quaternary arsonium, AsR_4^+. The cationic groups containing hydrogen such as $RNH_3^+Cl^-$, which is sometimes written as $RNH_2 \cdot HCl$, are weak bases and are stable only in the presence of acids. The quaternary ions all form strong bases and include some free bases which are stronger than sodium hydroxide and are completely ionized in solution.

Soaps include not only the salts of long chain fatty acids, to which the term was originally applied, but also many synthetic detergents which have soap-like qualities. Products such as Dreft, Duponol, Gardinol, Super-Suds, and other products with perhaps a thousand different trade names, all behave like soap in some respects. All of them lower the surface tension of water and most of them form suds. Many of them are effective cleaning agents and can replace soap for domestic uses. Figure 9–15 shows a collection of atomic models of various detergents including the laurate, oleate, and stearate ions which are present in classical soaps; lauryl sulfate which is sold as Dreft, Duponol, Santomerse and by other trade names; lauryl sulfonate and two cationic detergents, lauryl ammonium chloride, and lauryl pyridinium chloride.

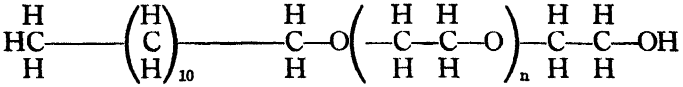
The properties of soaps and detergents depend to a large degree on the nature of the small counter-ion. Potassium and ammonium soaps are soluble in water at lower temperatures than sodium soaps. Soaps of heavy metals are usually insoluble in water and are unionized, but they may be soluble in oils.

There are a few non-ionic surface-active agents which are water soluble and have many of the properties of detergents. In the absence of an ionic group, several hydrophilic groups are necessary to produce a molecule with the properties of a colloidal electrolyte. The two hydroxy groups and the ester linkage of glycerol monolaurate give it many of the properties of a soap. Ether linkages have



$$H_3C(CH_2)_{10}C(=O)-O-CH_2-CH(OH)-CH_2OH.$$

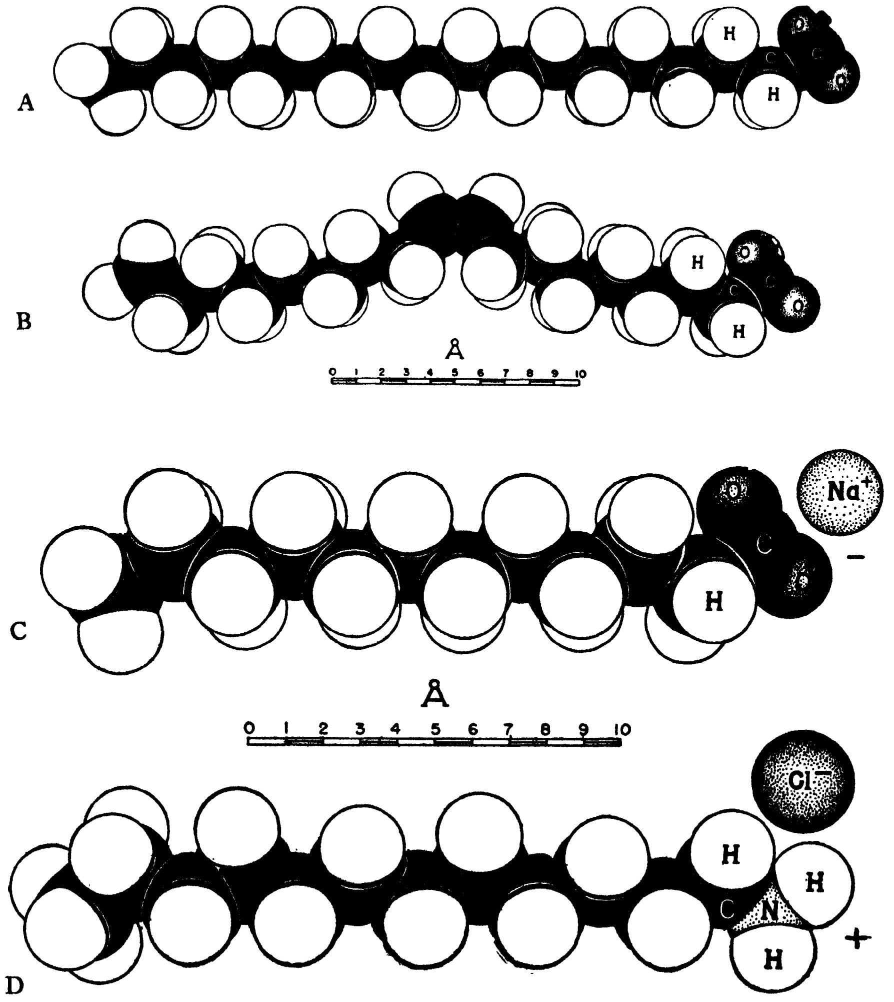
less affinity for water and the lauryl ether of polyethylene glycol must contain 8 or 10 glycol units before it is sufficiently water soluble.



$$H_3C(CH_2)_{10}CH_2-O(-CH_2-CH_2-O)_n-CH_2-CH_2-OH$$

These so-called nonelectrolyte detergents and wetting agents have not been investigated as carefully as have the soaps and some of the cationic detergents.

Solutions of Colloidal Electrolytes.—In very dilute solutions colloidal electrolytes are completely dissociated into their ions and behave as simple electrolytes which have the same effect on the colligative properties of the solution as does an electrolyte like KCl. As the concentration of a colloidal electrolyte is increased, the ions associate together to form micelles, which are particles of colloidal size



containing both organic ions and neutral soap molecules. When a solution which contains micelles is diluted, the micelles dissociate to form ions again.

The concentration above which a colloidal electrolyte contains micelles is called the critical concentration for the formation of micelles. The critical concentration can be obtained from measurements of conductivity or from measurements of one of the colligative properties of the solution, such as freezing point or vapor pressure. The colligative properties can be represented in terms of the osmotic coefficient, g. The osmotic coefficient represents the number of particles in solution expressed as a fraction of the maximum number which would exist if the substance were completely dissociated. Figure 9–16 shows the osmotic coefficient of potassium laurate as determined from the freezing point depression. At a concentration of 0.4 M, micelles begin to form and the value of g decreases because many of the ions unite to form micelles and each micelle behaves as a single particle.

When dilute solutions of potassium laurate are concentrated, the laurate ions associate together into micelles which may contain from 10 to 100 or more laurate ions and from 6 to perhaps 80 potassium ions. The micelles present in relatively dilute solutions probably contain fewer particles and a smaller proportion of potassium ions than the micelles which are formed in concentrated solutions. In concentrated solutions, containing more than 10% of soap, X-ray evidence indicates that potassium laurate molecules are arranged in parallel layers with water between the polar heads of the mole-

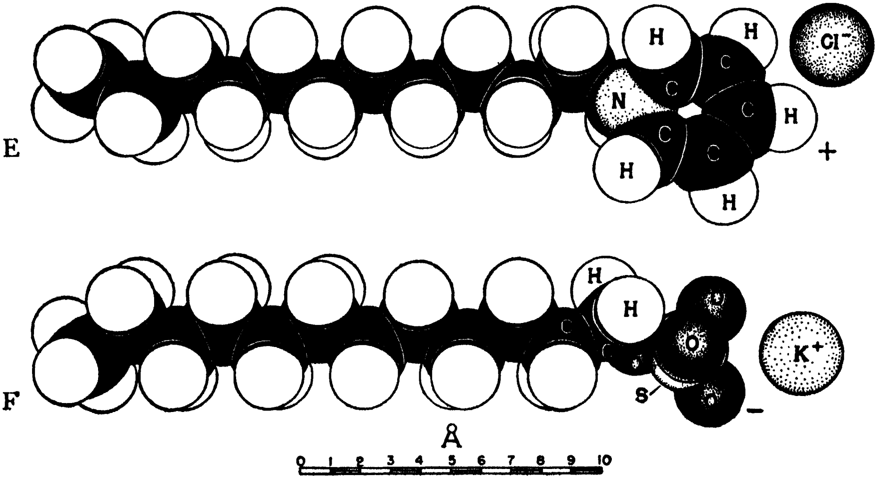


FIG. 9–15. Models of colloidal electrolyte ions. (A) Stearate, (B) Oleate, (C) Sodium laurate, (D) Lauryl ammonium chloride, (E) Lauryl pyridinium chloride, (F) Potassium lauryl sulfate.

cules. Figure 9–17a shows an idealized arrangement of the potassium laurate molecules in the micelle. The hydrocarbon tails are shown in a parallel arrangement, as they are in a crystal, but they undoubtedly are more randomly arranged, since they behave as a liquid.

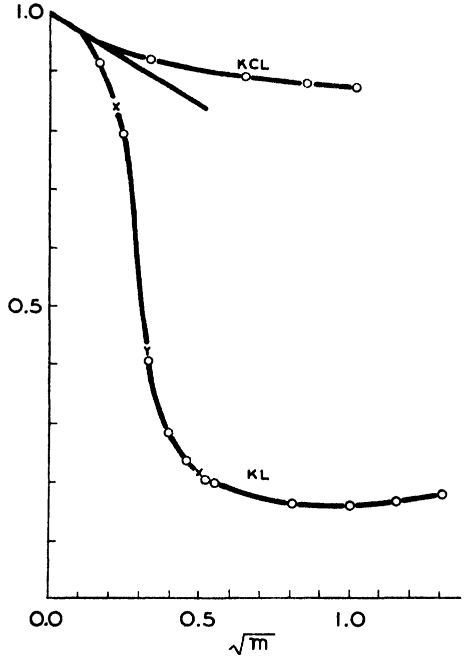


FIG. 9–16. The osmotic coefficient of potassium laurate. (From McBain, *Alexander's Colloid Chemistry* 5, Reinhold (1944).)

When an oil, which is insoluble in water, is added to a soap solution it is dissolved or "solubilized" by the soap solution. This is a perfectly reversible phenomenon, not to be confused with emulsification which is discussed in the next chapter. Solubilization occurs in any organic colloidal electrolyte which contains micelles. The oil is taken up as single molecules which are dissolved in the hydrocarbon tails of the detergent ions. Figure 9–17b shows, again very schematically, the structure of a potassium laurate solution saturated with an oil. X-ray evidence shows that the effective length of the hydrocarbon portion of the micelles is increased when an oil is added. There is no reason to suppose that all of the oil molecules are located in a layer which is free of laurate chains. On the contrary, one would expect the oil molecules to penetrate into the liquid hydrocarbon structure.

Oils, and other substances which are soluble in hydrocarbons, are solubilized by soap solutions to an extent which varies inversely with their molecular weight. Small molecules, such as benzene, are solubilized to a much greater extent than larger molecules, such as cetane, $C_{16}H_{34}$, and the solubilization of the common vegetable and animal oils, such as olive oil, is too minute to be detected.[6]

Some oil-soluble dyes, which are similar in structure to the dyes used to color butter and which contain two or three aromatic rings, are solubilized in quantities which can readily be determined by the color of the solution. According to a recent report from Harkins' laboratory,[7] a water-soluble cyanine dye, pinacyanol chloride, changes color when solubilized by soap micelles. The use of this dye will permit investigations of solubilization and the presence of micelles in solution, without introducing the difficulties which attend working in systems containing two phases.

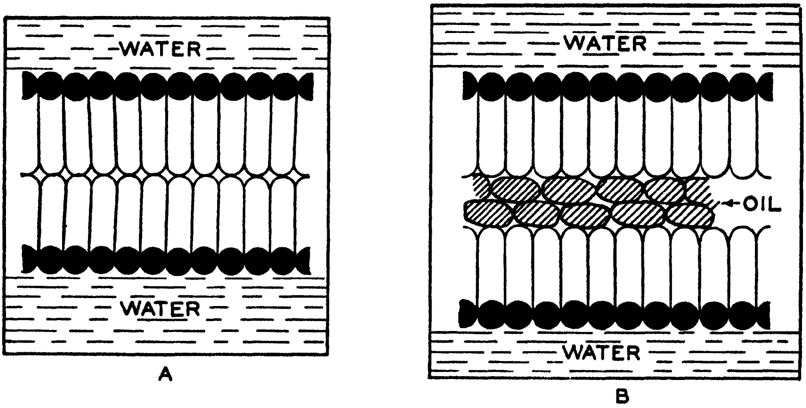


Fig. 9–17. Micelles in solutions of potassium laurate; (A) in water; (B) plus a solubilized oil. After Harkins, Mattoon and Corrin. *J. Colloid Sci.* **1**, 106 (1946).

Pure sodium and potassium soaps of fatty acids form clear solutions in water. For each soap there is a narrow temperature range below which the soap is insoluble and above which it is soluble up to a concentration of about 20% to 30%. The temperature at which a soap is soluble at about 20% concentration is influenced by the metallic ion which is present and by the length of the carbon chain. Potassium soaps are soluble at temperatures which are 30° to 40°

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[6] McBain, J. W., and Richards, P. H., *Ind. and Eng. Chem.* **38**, 642 (1946).
[7] Corrin, M. L., Klevins, H. B., and Harkins, W. D., *J. Phys. Chem.* **14**, 216 (1946).

lower than the temperature at which the corresponding sodium soaps are soluble. An increase in chain length of 2 carbon atoms increases the temperature of equivalent solubility by about 15°. Sodium laurate, $C_{12}H_{23}OONa$, becomes soluble in the range from 25° to 40° C., while sodium stearate ($C_{18}H_{35}OONa$) is insoluble below 60° and very soluble at 75°. Most commercial soap mixtures have solubility temperatures between 40° and 50° C.

In a concentration range between about 25% and 50% and above the solubility temperature, most soaps form a very sticky viscous phase known as the liquid-crystalline phase. This phase consists of partially oriented molecules of soap and water. It can be melted only by heating in a closed system under pressure to temperatures well above the boiling point of water. The liquid-crystalline phase is sometimes known as a soap jelly. Some commercial soap flakes are accompanied with instructions to disperse the flakes in a little cold water before adding hot water. In this way you can avoid the formation of large lumps of liquid-crystalline jelly which are difficult to disperse.

Soap and water systems containing more than about 50% soap are solids and are known as soap curds. There is a bewildering multiplicity of soap phases known and the student is referred to the publications of J. W. McBain, and R. D. and M. J. Vold for further information. For example see the paper by McBain, Vold and Porter.[8]

Applications of Colloidal Electrolytes.—The greatest use for colloidal electrolytes is as detergents for cleaning. We are all familiar with the uses of soap and water for cleaning our skin, our clothes, and our utensils. Soap solutions loosen the adhesion of dirt for other materials, and also help keep the dirt in suspension. There are many different types of dirt and many different base materials; yet soaps help to clean almost all types of soiled surfaces. It is not surprising, therefore, to find that there are many theories of the mechanism of detergent action and that soaps function in a variety of different ways.

Soaps solubilize oils of low molecular weight and emulsify almost all water-insoluble oily materials. Emulsification will be treated in greater detail in the next chapter; it is sufficient to say that the soap molecules form an oriented layer covering the oil droplets. The hydrocarbon portion of the soap is directed toward the oil, and the polar part of the soap ion remains in the water phase. The action of soap in removing solid particles which are covered with thin oily or greasy layers is a result of exactly the same type of orientation of the soap molecules.

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[8] McBain, J. W., Vold, M. J., and Porter, J. L., *Ind. and Eng. Chem.* 33, 1049 (1941). See also Vold, R. D., and Vold, M. J., *Alexander's Colloid Chemistry* 5, 266 (1944).

The mechanism by which soap aids in the removal of hydrophilic solid materials, such as clay and iron oxide, must be more complicated. The polar heads of the soap probably adsorb on the hydrophilic materials leaving the hydrocarbon tails outward. The particles now have a hydrophobic surface and are covered with a second layer of soap molecules in the same way that naturally greasy particles are covered.

The dual nature of a soap molecule, which possesses an oil-soluble portion and a portion solution in water, enables soap to sorb on to virtually every kind of material. McBain has illustrated the nature of detergency in the following word equation:

$$\text{Dirt-fabric} + \text{Soap} \longrightarrow \text{Dirt-soap} + \text{Fabric-soap.}$$

It should be noted that the soap adheres to the cleaned surface as well as to the dirt. When you wash your face with soap you exchange a covering of dirt for a covering of soap. Removal of the soap by rinsing may be difficult if the soap is strongly adsorbed.

Polyvalent cations, such as Ca^{++}, precipitate sodium soaps of fatty acids as an insoluble scum. Most household water contains some calcium ions and the water is more or less "hard." Hard water requires more soap than "soft" water which contains no Ca^{++} or Mg^{++} ions since soap must first be added to precipitate all the polyvalent ions, and enough more must then be added to function as a detergent. Hard water appears to rinse soap off more readily than soft water because the Ca^{++} ions in the water precipitate the soap in the fabric or on the skin of the user.

The soaps of sulfated fatty alcohols, $ROSO_3^-$, are much less sensitive to the action of Ca^{++} and Mg^{++} ions and these soaps will produce suds in hard water. Furthermore, these soaps are the salts of strong acids, and they remain ionized in neutral or weakly acid solutions. The fatty acid soaps must be used in alkaline solutions to keep the free acid from precipitating.

Soaps which consist of sulfated esters are slowly hydrolyzed in acid solutions forming fatty alcohols and the sulfate ion. They should accordingly not be used in strongly acid solutions for any length of time or at high temperatures. The cationic detergents, such as lauryl ammonium salts, are quite stable in acid solutions, but will revert to the fatty amine and chloride ions in neutral or basic solutions. The quaternary amines, however, are stable in neutral solutions. A mixture of a cationic detergent with an anionic detergent frequently leads to salt formation and precipitation, and it is inadvisable to mix detergents of opposite sign. Cationic detergents are sorbed more strongly than anionic detergents on surfaces such as cotton and silk which have free anionic groups.

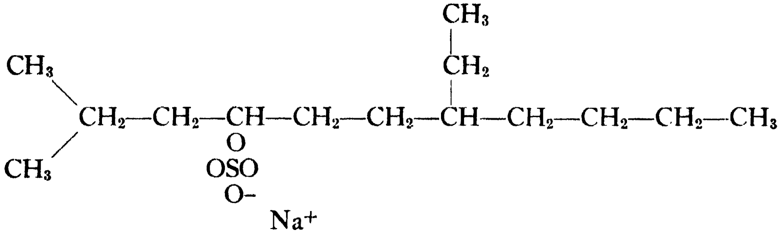
Micelle formation in detergents is promoted by the presence of excess counter-ions. This is simply a "common ion" effect, the presence of excess Na^+ ions for example favors the reaction which produces micelles.

$$x\mathrm{Na}^+ + y\mathrm{RCOO}^- \longrightarrow (\mathrm{Na})x\,(\mathrm{RCOO})y^{(y-x)-}.$$

The micelle behaves very nearly as if it were a separate phase which exists in equilibrium with the dissolved soap ions. Salts are frequently added to commercial detergents to function as "builders" or promoters of micelle formation. Fatty acid soaps frequently contain added sodium silicate or sodium phosphate. The sodium ions act as builders, and the basic anions help maintain a high pH and also remove calcium ions. Some of the polyphosphates appear to inhibit the formation of precipitates of calcium salts. Sulfated and sulfonated detergents usually contain sodium sulfate. These compounds are made by the action of sulfuric acid on suitable organic precursors, and the excess sulfuric acid is simply neutralized with sodium carbonate and left in the product. These detergents can be purified by extracting them with alcohol, which does not dissolve sodium sulfate, and if necessary, by subsequently extracting the unreacted higher alcohol and possible hydrocarbons with ether which does not dissolve the sulfates.

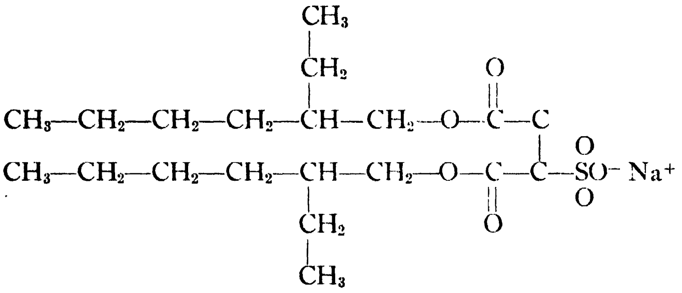
Wetting agents are substances which lower the contact angle between water and hydrophobic surfaces. Wetting agents have a structure similar to the structure of soaps and detergents in that they have a polar and a non-polar portion. They lower the contact angle because their hydrocarbon-like tails sorb onto the non-polar surfaces, and their polar groups attract water. Many detergents are also good wetting agents and *vice versa*. It has been found, however, that straight chain compounds with a polar group at one end make the best detergents, whereas branched compounds or chains with a polar group near the middle make the best wetting agents.

Wetting agents are frequently tested by a sinking test in which a piece of unwashed cotton is weighted with a plummet and placed in the wetting agent. The rate at which the cotton sinks is a measure of the wetting ability of the agent. Among the more effective wetting agents are sulfates of secondary alcohols and sulfosuccinate esters. The first group, which includes some of the Tergitols, are represented by formulas such as the sodium sulfate of 2-methyl-7-ethyl undecanol-4 (Tergitol 4)



$$\begin{matrix} & & & & & & CH_3 & & & \\ & & & & & & | & & & \\ CH_3 & & & & & & CH_2 & & & \\ & \diagdown & & & & & | & & & \\ & & CH_2-CH_2- & \underset{\substack{O\\OSO\\O^-\\ \quad Na^+}}{CH} & -CH_2-CH_2- & & CH & -CH_2-CH_2-CH_2-CH_3 & & \\ & \diagup & & & & & & & & \\ CH_3 & & & & & & & & & \end{matrix}$$

The second group is known by the trade name of Aerosols.[9] Aerosol OT, 2-ethyl-hexyl sodium sulfosuccinate,



$$\begin{matrix} & CH_3 & & & \\ & | & & & \\ & CH_2 & & O & \\ & | & & \| & \\ CH_3-CH_2-CH_2-CH_2- & CH & -CH_2-O- & C & -C \\ & & & & |\quad O \\ CH_3-CH_2-CH_2-CH_2- & CH & -CH_2-O- & C & -C-SO^-\ Na^+ \\ & | & & \| & \quad O \\ & CH_2 & & O & \\ & | & & & \\ & CH_3 & & & \end{matrix}$$

is one of the most powerful wetting agents known. Aerosols are made by treating the esters of fumaric acid, ROOC—CH=CH—COOR, with a chemically equivalent amount of sodium bisulfite, $NaHSO_3$, which adds to the double bond to produce the sulfosuccinate. Figure 9–18 shows atomic models of the two compounds described above.

Many detergents and related compounds are used as dispersing agents to keep powdered particles from sticking together in the presence of solvents. These agents are particularly effective in nonaqueous systems. Good dispersing agents reduce the rate of settling of finely divided pigment powders in oils because they keep the particles from sticking together. When the particles stick together, or flocculate, the effective radius of the unit increases and the substance settles more rapidly. In concentrated paste-like sys-

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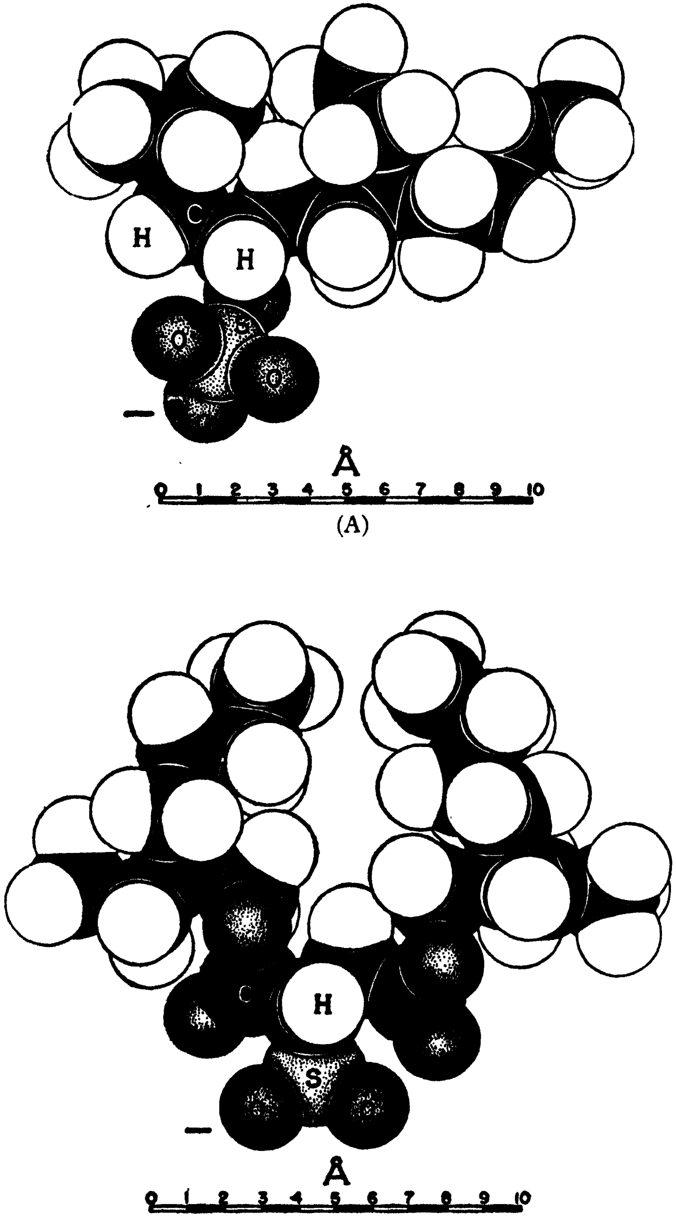
[9] Aerosol is a trade name for a series of detergents. See also p. 271.



(A)

(B)

Fig. 9–18. Models of (A) Tergitol 4, and (B) Aerosol OT.

tems, dispersing agents improve the working qualities and the flow characteristics of the mixture.

Lubricating greases are light oils suspended in a gel framework which consists of a soap stabilized by a small quantity of water. Different soaps may be used for special purposes. Sodium soap greases are dispersed by water whereas aluminum soaps are very resistant to water. Ordinary cup grease contains calcium soaps of the longer fatty acids, especially calcium stearate, $Ca(C_{18}H_{35}OO)_2$. Lithium soap greases are a recent addition which are remarkably water resistant and can be cooled to low temperature without too great an increase in stiffness.

A grease serves as a reservoir of lubricating oil which is held in a gel structure where it can be taken up by the bearing surface as needed. The grease structure may also persist between the bearing surfaces in some cases. Some of the soap molecules may be sorbed as a monolayer on the bearing surfaces. The polar heads would stick to the metal leaving the hydrocarbon tails to serve as points of adhesion for the oil layer between the surfaces. Many lubricants contain surface-active additives to increase their lubricating power. Other agents may also be added to disperse sludge and carbon particles, and prevent them from adhering to the metal surfaces of the engine.[10]

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[10] Bonner, C. J., "Lubricating Greases as Colloidal Systems," *Alexander's Colloid Chemistry* **6**, 553 (1946).

CHAPTER 10

EMULSIONS AND FOAMS

General Considerations.—An emulsion consists of small drops of one liquid suspended in another liquid. As was pointed out in Chapter 1, the drops of most emulsions are larger than 1000 Å, and emulsions are classified as colloids only because they require the presence of colloidal material to make them stable. It is frequently very hard to distinguish between a true emulsion containing liquid drops and a suspension of a soft or easily melted solid. Photographic "emulsions" are dispersions of solid silver halides in gelatine and should not be called emulsions at all. On the other hand, the blood is not usually called an emulsion, although some of the properties of the red blood cells suggest that their contents are fluid.

It is possible to disperse one pure liquid as droplets in another pure liquid, but the dispersion is unstable and the liquids usually separate fairly rapidly. All stable emulsions consist of at least three components, two immiscible liquids and a stabilizing agent. Very dilute emulsions of oils in water may form lyophobic colloidal systems similar in all respects to the lyophobic solutions which are discussed in Chapter 12. The stabilizing agents in these emulsions are frequently hard to identify; they are usually ionic groups which are present on the surface of the emulsion droplets.

The vast majority of emulsions met with in practice contain more than 1% of the more dilute phase. Most of the useful ones contain a stabilizing agent which has been intentionally added to the system. If you shake together approximately equal volumes of benzene and water, both liquids will break up into drops and the mixture will contain drops of water, which are surrounded by benzene, and drops of benzene, which are surrounded by water. It is even possible to find a few droplets of water inside drops of benzene which are in turn surrounded by water. This mixture of benzene and water drops is unstable and whenever two benzene drops touch they will coalesce to form a larger drop. When you stop shaking the bottle the benzene drops will continue to grow in size and will rise through the water to form a layer of benzene. Likewise water drops will coalesce and sink through the benzene until the mixture has separated into two layers.

If you shake benzene with a dilute soap solution, such as 1% sodium oleate, each drop of benzene will become covered with a sorbed layer of oleate ions, all oriented with their hydrocarbon tails in the benzene and their ionic groups in the water. The surface of the benzene drop will resemble a soap micelle (see Figure 10–1). When two benzene drops collide, the soap ions will not stick together and the drops will bounce apart again. A well-prepared emulsion of benzene in sodium oleate solutions may be stable for a long time.

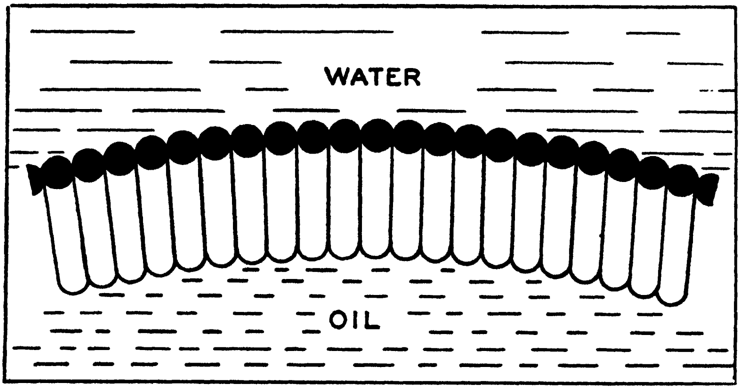

FIG. 10–1. Orientation of the stabilizing molecules in oil-in-water emulsions.

Any emulsion is inherently unstable and will eventually break down to form two layers. Emulsions are unstable because the system has a large interfacial surface area and an interfacial surface energy which is proportional to this area. A change in the system which reduces the total surface energy will bring the system into a more stable state. The total surface energy is reduced if the emulsion drops coalesce, because the surface area is reduced when two drops join to make one drop. The surface energy is equal to the product of the area, A, and the interfacial tension, γ_{01}. Soaps and other surface active agents which sorb on the interface reduce the interfacial tension below 10 dynes per cm at a concentration of 0.2% (see Figure 3–9). Many surface active agents reduce the surface tension below 1 dyne per cm and some oil droplets in living cells have been found to have an interfacial tension as low as 0.1 dyne per cm.[1]

One way in which surface active agents promote the stability of emulsions is by reducing the total surface energy of the system.

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[1] Harvey, E. N., and Danielli, J. F., *Biol. Rev.* **13**, 319 (1938); and Kopac, M. J., *Cold Spring Harbor Symposium on Quantitative Biology* **8**, 154 (1940).

Willard Gibbs pointed out that any substance which lowers the surface tension will be concentrated at the surface. Surface active agents, therefore, will always cover the surface of whatever emulsion drops are present and may serve as protective layers which prevent two drops from coalescing when they collide. Some proteins are sorbed and denatured at oil-water interfaces and the denatured film has considerable rigidity. An emulsion stabilized by rigid films may be very stable for so long as it is left undisturbed. It may have a long "shelf life" but, since rigid films are brittle and cannot build up again once they are broken, such an emulsion may have a very poor "service life."

The lower limit of size of emulsion droplets is frequently determined by the concentration of the stabilizing agent. Emulsion droplets which are not completely covered with a condensed monolayer of a stabilizing agent are unstable, and usually coalesce until the total surface area equals the cross-sectional area of the molecules of the stabilizing agent.

For example, most straight chain surface-active agents, such as the oleate radical, have a cross-sectional area of about 20 square Å. The area per mol of oleate radicals is 20 $Å^2$ times Avagadro's number, or 20×10^{-16} cm^2 $\times 6 \times 10^{23}$ which is 1.2×10^9 cm^2. One mol of sodium oleate weighs 304 gm. One cubic centimeter of a 1% solution therefore contains 0.01 gm or 3.3×10^{-5} mols. The area which could be covered by this quantity of oleate radicals is $3.3 \times 10^{-5} \times 1.2 \times 10^9$ cm^2 or very nearly 4×10^4 cm^2. An emulsion containing equal parts of benzene and water would contain 1 cc of benzene to each cubic centimeter of water. If this volume were distributed in spheres with a total area of 4×10^4 cm^2 the mean diameter would be

$$d = 6V/A. \qquad (10\text{–}1)$$

Therefore $d = 6 \times 1.0/4 \times 10^4 = 1.5 \times 10^{-4}\text{ cm} = 1.5\mu$.
A diameter of 1.5μ represents an emulsion droplet size which can be obtained fairly readily by the use of good homogenizing equipment such as is described later in this chapter.

Benzene and water were chosen as examples of liquids which are not miscible with each other and which form emulsions when they are mixed together. Any other liquid which is not completely miscible with water can be used to make an emulsion in water. Organic liquids which are immiscible with water are usually called oils by emulsion technologists. The lower alcohols and glycols behave like water in emulsions. An emulsion which consists of oil drops dispersed in a continuous water phase is called an oil-in-water emulsion. This term may be expressed by the symbol O/W. Likewise an emulsion of water drops in oil is called a water-in-oil emulsion with the symbol W/O. Mixtures of these two types of emulsions are rarely stable and are hardly ever found in practice.

The stabilizing agent is the principal factor which determines whether an emulsion will be O/W or W/O. A mixture of benzene in dilute sodium oleate produces emulsions of the O/W type which contain benzene droplets surrounded by sorbed oleate ions and floating in an aqueous solution of sodium and oleate ions.

Many attempts have been made to formulate rules which will predict the kind of emulsion that will be produced by a given emulsifier. The most generally useful rule is that the phase in which the stabilizing agent is most soluble will be the external phase. Soaps of the alkali metals or ammonia are soluble in water and insoluble in benzene at room temperatures and therefore water forms the external phase when sodium oleate or similar soaps are the stabilizing agents. Soaps of divalent metals are insoluble in water but soluble in oils, so that an emulsion stabilized with calcium oleate will be of the W/O type. There are a few exceptions to this rule. Some phospholipids which are soluble in ether, and nearly insoluble in water, nevertheless stabilize emulsions of the O/W type. Although there are a few other exceptions to this rule, it still gives the best indication of the type of emulsion to be expected from a given set of components.

Aqueous solutions of sodium oleate can be converted to insoluble calcium oleate by the addition of a soluble calcium salt. When a calcium salt is added to an O/W emulsion, which is stabilized by sodium oleate, the soap is converted to the oil-soluble calcium oleate and the emulsion may be inverted to the W/O type. Inversion of emulsions frequently breaks some of the emulsion and produces layers of the two liquid components. When the calcium and sodium ions are present in a critical ratio (about 1:20) the emulsion may be completely broken.

✓One very popular theory which attempts to predict the kind of emulsion that will be produced by a given stabilizing agent is known as the "oriented wedge" theory. This theory was developed by Harkins and by Hildebrand from the fact that emulsifying agents cover the surface of the drops with a mono-layer of sorbed material. They assume that a carboxylate ion has larger cross-sectional area than a hydrocarbon chain and therefore that a layer of sodium oleate, for example, would tend to curve toward the oil phase and produce an O/W emulsion. If, however, two oleate radicals are attached to a single small calcium ion, the pair of hydrocarbon chains would be larger than the polar head, and a layer of calcium oleate would curve toward the aqueous phase and produce a W/O emulsion.

Although this theory does predict the kind of emulsion that will be produced with soaps it is incomplete and leaves many facts unexplained. Furthermore the radius of emulsion drop is from 100 to 10,000 times as great as the length of a soap molecule and it is unlikely that the wedging effect could be the only factor which determines whether an emulsion will be O/W or W/O.

Oil-in-water emulsions are stabilized by most water-soluble high polymers, including proteins and water-soluble colloids related to the carbohydrates such as gum arabic and sodium alginate. Rubber nitrocellulose and the oil-soluble resins are usually good stabilizing agents for W/O emulsions. Many other organic high polymers which possess a few polar groups will probably also stabilize W/O emulsions. Likewise the water-soluble high polymers such as polyethylene glycol and polyvinyl alcohol are good stabilizing agents for O/W emulsions.

It is not always easy to distinguish O/W emulsions from W/O emulsions by visual observation. The "feel" and behavior of the two types are usually different but it takes an experienced operator to make use of these properties. Emulsions which have water as the continuous phase can be diluted with water but not with oils. Water-soluble dyes, such as ink, diffuse rapidly through most O/W emulsions. The electrical conductivity of O/W emulsions is usually high. Water-in-oil emulsions, on the other hand, mix with oils and with oil-soluble dyes such as Sudan III and commercial butter and margarine dyes. Oils are very poor conductors of electricity and the conducting water droplets are insulated from each other in W/O emulsions; therefore these emulsions have low electrical conductivity.

Some finely divided powders will also stabilize emulsions. For a powder to stabilize an emulsion it must be wet by both liquids. The liquid which wets the powder more strongly will be the external phase. This rule is merely an extension of the general rule regarding the stability of emulsions. Figure 10–2 shows how solid particles can stabilize an emulsion. Soot, which is wet more easily by oil than by water, stabilizes W/O emulsions. Silica powder, which is wet more easily by water than by oil, forms O/W emulsions. Some mixtures of soot and silica will not protect emulsions of either type.

The choice of an emulsifying agent is determined by the service to be expected from the emulsion. Food products must be stabilized by nontoxic substances. The natural colloids of eggs, which include albumin in the white and phospholipids in the yolk, have long been used to prepare emulsions for human consumption. Mayonnaise is an emulsion of a vegetable oil in an aqueous solution of vinegar and flavoring substances. It is stabilized by the phospholipids and proteins of egg yolks. "Salad dressing" may include other stabilizing agents such as alginates, starch or gums and it is possible to make a salad dressing which is much more stable than mayonnaise.

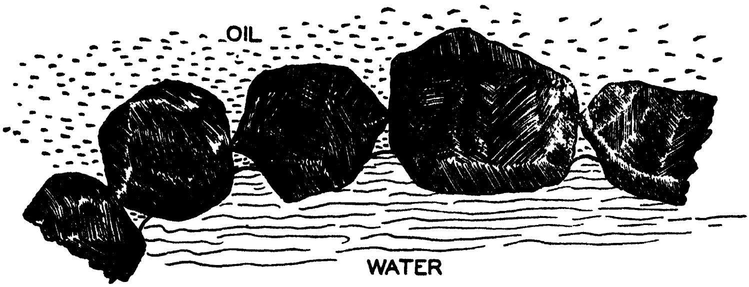

FIG. 10–2. Part of the surface of an emulsion drop stabilized by soot.

Milk and Butter.—Milk is an emulsion of butter fat in an aqueous solution of proteins, milk sugar and salts. Most of the emulsion droplets in cows' milk are from 3 to 10μ in diameter. They are stabilized by a complex protein and phospholipid film which has an electrophoretic mobility different from that of any of the common proteins of milk. The individual fat droplets are lighter than the milk serum and rise slowly under the influence of gravity. A fat droplet 3.3μ in diameter will rise at a rate of 0.18 cm per hour or 1 in. in 14 hours. However, cream rises much more rapidly than this because the fat globules aggregate together to form larger clumps which contain about 50% of butter fat. The rate of rise of cream can be accelerated by centrifuging the milk. A modern cream separator exerts a force of 1000 times gravity and continuously removes most of the cream from a stream of milk that is flowing steadily through it.

The protective film around the fat particles in cream can be broken and coagulated by beating air into the cream at temperatures between 5° and 20° C. Butter fat is a liquid at body temperatures and has an indefinite "melting point" near room temperature. In order to churn cream to butter it is necessary to work at a temperature where butter fat is solid. Churning is a process of beating air into cream, for 20 to 30 minutes, until the fat particles stick together and become butter. Butter contains up to 15% of entrained water, which carries the salt used for flavoring, as well as minute air bubbles.

When butter is melted the fat separates from the air and water, and when the melted fat is cooled it sets to a waxy solid which is very unlike the original butter.

Rubber Latex.—Rubber occurs as latex in the sap of several species of trees and plants. Latex, so called because it resembles milk, is called an emulsion even though the rubber particles are very nearly solid. Latex, as it comes from the *Hevea braziliensis* tree of the East Indian plantations, contains about 35% rubber and 2% of proteins. The particles are about 1μ in diameter and usually have a teardrop shape. The pH of latex as it comes from the plant is about 7. The protein in the latex, which protects the latex particles, is unstable and latex coagulates if the pH falls below 6. Bacterial action in freshly drawn latex produces organic acids which will coagulate the latex. Other acids are frequently used to coagulate latex on large plantations since this produces a more uniform product.

Latex is stable in the presence of 1% ammonia and can be shipped after some of the water has been removed to reduce transportation charges. The particles of rubber latex are so small that they rise very slowly. Latex can be concentrated in centrifuges similar to milk separators. The particles may also be agglomerated by certain water-soluble colloids such as Irish moss or pectin. These colloids make the rubber particles stick together so that they will rise rapidly to produce a cream containing about 55% rubber.[2]

When rubber latex is coagulated the protective films around the particles break and permit the rubber to flow together as a single mass. Two clean surfaces of rubber will likewise stick together because the molecules are in motion and can intertwine with molecules from the other side of the joint.

Rubber latex is used as an adhesive and for making thin rubber goods. The shortage of natural rubber in World War II led to the development of several synthetic latex substitutes. One fairly successful adhesive emulsion was composed of polyvinyl acetate. Thiokol was the most successful of the synthetic rubbers for use in latex form. Latex can be extruded into a coagulating bath to form threads such as Lastex. Rubber emulsions can also be "electroplated" because the particles are covered with a negatively ionized protein. The rubber, therefore, migrates to the anode where it sticks. The proteins may be coagulated by the acids or salts which are formed on the anode by electrolysis. Freshly deposited latex is still porous but when dried the particles fuse together to make a strong, coherent, airtight sheet the exact shape of the anode. These thin sheets can be vulcanized by the external application of vulcanizing agents, such as a solution of sulfur monochloride, S_2Cl_2; or the vulcanizing agents can be incorporated in the latex before it is deposited. Thin rubber articles are also made by dipping the mold in latex. To reduce drainage, the latex may be made plastic by the addition of bentonite which is thixotropic and sets rapidly to a gel as the mold is removed.

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[2] Van Gils, G. E., and Kraay, G. M., *Advances in Colloid Science* 1, 247 (1942).

Foams.—Foams are similar to oil-in-water emulsions in which the oil is replaced by air or the vapor of the foaming liquid. Foam bubbles are usually of visible dimensions, rarely being less than 0.1 mm in diameter. The continuous phase may be reduced in a drained foam to 0.01% or less of the total volume. Even in such thin layers some foams behave as if they were two-dimensional liquids which can flow about on the surface but which resist any force which tends to make them thinner.

Like emulsions, all foams must be protected by a stabilizing agent. There are theoretical and experimental reasons for believing that simple liquids do not foam when pure. It is not easy to prove this statement because stabilizing agents may be present as impurities and some substances stabilize foams when they are as dilute as 0.001%.

Foams in water are produced by many salts. These foams are not particularly stable but they may be troublesome in steam boilers where they cause "priming" or entrainment of water in the steam. Foams of this type have been most extensively studied by Foulk.[3] Surface active agents of low molecular weight, such as the higher alcohols and acids, also produce foams but the best and most stable foams are produced by colloidal substances such as proteins and soaps. Beaten egg-white is a very familiar protein foam, and the foam on beer is caused by degraded proteins. Soap suds and soap bubbles are perhaps the best known and the most extensively studied of all foams.

Soap bubbles present a fascinating field of study. A soap bubble film is only a few thousand Å thick and yet the different parts of the film are usually in continuous motion. Films which have a thickness of the order of the wave length of visible light will show brilliant iridescent colors. These colors are the result of interference of light waves reflected from the inner and outer surfaces of the bubble. Interference reduces the intensity of those colors whose wave lengths are equal to four times the thickness of the film and we see the colors which are left. Thicker films show less brilliant colors, and films thicker than 10,000 Å (1μ) are clear, colorless, reflecting films. Some soap bubbles have so-called black areas which do not reflect light because the film in these areas is too thin to cause interference of visible light.

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[3] Foulk, C. W., *Ind. and Eng. Chem.* **21**, 815 (1929); **23**, 1283 (1931).

Some soap bubble films appear to be made up of platelets which are about 50 Å thick. Since the color of a soap-bubble film depends upon the thickness, the presence of two different colors with a sharp line between them proves that the thickness changes abruptly at that line. Much as this subject has been studied, there is still no satisfactory theory of the structure of a soap bubble. We do not know why it can be so fluid and so thin and yet resist further decrease in thickness.

The traditional recipes for soap bubbles employed glycerine along with the soap to produce tougher, more brilliant bubbles. Some of the newer synthetic detergents produce soap bubbles which are superior to the old-fashioned soap and glycerine bubbles. Glycerine substitutes are also employed in some soap bubble recipes.

Solids may be attracted to an air-water interface just as they are attracted to an oil-water interface. Many important minerals can be treated with surface-active agents and then concentrated in a foam or froth produced by blowing air into the mixture. This is the basis of the flotation process for concentrating low-grade ores. A particle will be attracted to the interface if its surface is less polar than the water. Various surface active agents are sorbed on the surface of ores, rendering their surfaces hydrophobic. Different minerals will react with different surface active agents so it is possible, by suitable choice of agents, to separate a complex mixture of minerals. Very few general rules can be formulated and each new ore is a problem in itself.[4]

Some Properties of Emulsions and Foams.—Most organic liquids are lighter than water and the droplets of an O/W emulsion will slowly rise under the influence of gravity until they touch each other. This process is known as creaming. The rate of creaming of discrete drops varies inversely as the diameter of the drop, as would be predicted from Stokes' law. Creaming may be accelerated by clumping of the drops to form larger aggregates. Emulsions which contain drops smaller than 1000 Å (0.1μ) may remain permanently dispersed by the action of convection currents in the body of the liquid.

[4] Gaudin, A. M., *Alexander's Colloid Chemistry* **6**, 493 (1946); also Hassialis, M. H., *Annals of the New York Academy of Sciences* **46**, 495 (1946).

A collection of uniform rigid spheres can pack together until the spheres occupy about 75% of the total volume. A mixture of large and small spheres can occupy a larger part of the total volume because the small spheres can pack between the large spheres. The cream layer of relatively homogeneous emulsions frequently contains about 75% of the dispersed phase although some emulsions, notably milk, produce a cream layer containing less than 50% of butter fat. It is possible to make emulsions of oil in water in which 99% of the volume is occupied by the oil. Such emulsions are stiff and jelly-like and the dispersed phase must have a high degree of rigidity. The structure of a concentrated O/W emulsion may be compared to that of a foam. If we consider the air as representing the oil phase, a foam can be made which is 99.999% air and contains only 0.001% of the aqueous phase.

Some oils are heavier than water and emulsions of these oils cream downward. It is possible to prepare a mixture of carbon tetrachloride, and benzene which has the same density as water. If this mixture is emulsified in water it will not cream either up or down. Water-in-oil emulsions usually settle or cream downward but again it is possible by suitable choice of densities to prepare emulsion drops which will either rise or sink.

Emulsions of finely divided drops appear white and creamy because light is reflected from all the interfaces in all directions. The amount of light reflected from an interface depends upon the difference in the refractive indices of the two phases. Just as it is possible to adjust the density of the two phases to prevent creaming, it ought to be possible to adjust the refractive indices to prevent light scattering. Transparent emulsions can be prepared in this way if the optical dispersive power is similar in the two phases. If the dispersive power is very different, the refractive indices will match at only a single wave length. Light of other wave lengths will be scattered and the emulsion will be colored. An emulsion of this sort is known as a chromatic emulsion. Instructions for making chromatic emulsions will be found in Holmes' *Laboratory Manual of Colloid Chemistry*.[5]

Methods for Producing Emulsions and Foams.—The production of a good emulsion is an art that requires skill and care to achieve uniform results. Many of the instructions for making emulsions may seem unduly complicated, and only actual experience can demonstrate the large differences which can occur as the result of seemingly minor changes in procedure.

The simplest way to make an emulsion, and one of the poorest, is to mix together all the ingredients in a bottle and shake it. Briggs[6] found that continuous shaking was less efficient than intermittent shaking in producing an emulsion of benzene in 1% sodium oleate. An illuminating experiment may be performed by placing 80 ml of benzene and 20 ml of sodium oleate in each of two 250 ml flasks. One flask is shaken continuously while the other is given one hard shake every 30 seconds. At the end of about 4 minutes the flask which has been shaken continuously is still not completely emulsified whereas the flask which was shaken intermittently has formed a white creamy emulsion.

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[5] Holmes, H. N., *Laboratory Manual of Colloid Chemistry* (1935).

Many emulsions are made by adding a slow stream of the inner phase to a small amount of the external phase containing all of the stabilizing agent. The two phases are thoroughly mixed and additional quantities of the external phase are added when necessary. Care is taken to keep the external phase always in excess of the internal phase. Mixing may be done by a stirring propeller or paddle or by an egg beater. A more elaborate method is to pump the emulsion continuously through a pump and back into the mixing chamber. There are many different types of emulsifying machines on the market which are known as emulsifiers, colloid mills, and homogenizers.

A homogenizer is a machine which reduces the size of the emulsion droplets. A centrifugal pump which operates at high speeds with small clearances is a good homogenizer. The small homogenizers which are designed to prepare cream from skim milk and melted butter are single cylinder pumps. The discharge from the pump passes through a small hole in which a spring-loaded valve operates. When a coarse emulsion is forced through under high pressure the valve will open and shut many thousands of times a second and will break up the emulsion into much finer particles. Homogenized milk contains fat globules which are less than 1μ in diameter. Particles this small do not cream on standing. Very few homogenizers will produce droplets smaller than 0.1μ in diameter. The smaller a drop is the greater must be the velocity gradient in the liquid to tear it apart.

The so-called Continental or European method of making pharmaceutical emulsions consists of grinding the dry emulsifier—for example, gum arabic—with the oil that is to be the inner phase until the oil is reduced to fine drops mixed with the powdered gum. Water is now ground into the mixture where it dissolves the gum and produces a fine emulsion. Silica, or other easily pulverized solids, may be ground with the oil, and the stabilizing agent can then be added in solution. If silica is used the powder remains in the emulsion; if sugar is ground with the oil it remains in solution in the aqueous phase. The success of the Continental method depends upon the fact that much greater shearing stresses can be exerted on the oil by solid particles than can be exerted in completely liquid systems, except perhaps in a colloid mill.

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[6] Briggs, T. R., *J. Physical Chem.* **24,** 120 (1920).

One of the most efficient methods of making a soap stabilized emulsion is to make the soap *in situ*. Fatty acid is dissolved in the oil which is then mixed with an aqueous suspension of an alkali. The acid will react with the base at the oil-water interface and the interfacial tension will be lowered to values close to zero. In some cases emulsification is spontaneous which indicates a negative interfacial tension. For example, 80 ml of 0.2% oleic acid in benzene is completely emulsified in 20 ml of dilute ammonium hydroxide by a single hard shake in a 250 ml flask. Some asphalt emulsions for use on roads are prepared by running molten asphalt, which contains natural naphthenic acids, into dilute alkali.

Emulsions can also be prepared by dissolving one phase in a substance which will dissolve both and then pouring the mixture into a large excess of the other phase. An oil may be dissolved in alcohol or acetone and this solution, when poured into water, will produce an O/W emulsion. The aqueous phase contains nearly all of the alcohol or acetone. If an O/W emulsion is prepared in this way the drops will soon coalesce and settle out unless a stabilizing agent is present. A somewhat similar method involves blowing the vapors of an oil, such as analine, into water with the aid of steam. This method produces unwanted emulsions when aniline is steam distilled, and impurities in the aniline stabilize the resultant emulsion. Emulsions are also produced when the solubility of one phase in a mixture is reduced, either by lowering the temperature or by adding a nonsolvent. The amount of water in an ester solvent can be estimated from the quantity of hydrocarbon which will mix with it without producing a fine emulsion or cloud. A similar test is carried out by reducing the temperature of a mixture until one component separates out as a cloudy emulsion.

Foams are usually prepared by blowing air (or some other gas such as carbon dioxide) through small holes immersed in the liquid. Sintered glass or porous earthenware or Alundum bubblers are available for the purpose of breaking up the air and producing small bubbles. Foams can also be produced by directing a jet of water into the solution. The water carries air bubbles with it and these rise through the solution and produce foams like those on a bathtub. An egg beater produces very good foams but must be used with care since many foams are broken by too much agitation.

Foams can also be produced by reducing the pressure on a dissolved gas. The foam on beer and other effervescent beverages is produced in this way. An essentially similar method is to produce the gas in the liquid by mixing solutions which will react to liberate a gas. The foam type of fire fighting apparatus produces foam by the reaction of a bicarbonate with an acid in the presence of a colloidal stabilizing agent. Bubbles will be formed in a liquid only if bubble nuclei are present, or if the liquid is rapidly agitated. Bubble nuclei consisting of small bubbles or layers of sorbed air are ordinarily present on dust particles in all exposed liquids. They can be removed by special techniques which remove the nuclei or dissolve the air. Many bottled effervescent drinks are free from bubble nuclei and if opened with care will not produce bubbles. Bubbling can always be started by sufficiently severe agitation.[7]

Methods of Breaking Emulsions and Foams.—Emulsions and foams are, more frequently than not, undesirable products in chemical processes. Emulsions prevent the separation of phases and recovery of the desired product, as in the case of aniline mentioned earlier. Foams may greatly increase the volume of a system which is being mixed and make necessary the use of much larger containers. A soap which foams excessively may remove most of the water from some types of washing machines as a wet foam. Solutions which foam are difficult to distill or evaporate. It is also difficult to prepare exact volumetric solutions of strongly foaming substances unless great care is taken to avoid entraining air while the solution is being mixed.

Emulsions and foams can be broken by destroying or removing the stabilizing agent. This sounds simple but may be difficult to carry out. Soaps can be converted to oil-soluble fatty acids by the addition of strong acids, and O/W emulsions which are stabilized by a soap can be broken in this way. Polyvalent cations can also be used, and in some cases even saturated salt solutions will make the soap so insoluble that it is no longer an effective stabilizing agent. Care must be taken when using these agents to prevent the formation of an inverted emulsion. Just the right amount of $CaCl_2$

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[7] Dean, R. B., *J. Applied Physics* **15**, 446 (1944); also Harvey, E. N., and others, *J. Am. Chem. Soc.* **67**, 157 (1945).

will break an O/W emulsion which is stabilized with common soap, but an excess will produce an inverted W/O emulsion.

Emulsions which are stabilized by proteins are harder to break, although some proteins can be rendered ineffective as stabilizers by a change of pH or by the addition of salts. The protein film which is sorbed on the oil-water interface is frequently in the insoluble, denatured form and it may therefore be impossible to remove it by agents which would precipitate the native protein. Air surfaces may, however, compete for the protein, and cream emulsions are broken to produce butter in a churn because the protein has been preferentially sorbed on air bubbles. Proteolytic enzymes occasionally can be used to advantage to break protein-stabilized emulsions, and in some instances bacterial putrefaction, although smelly, is effective. Emulsions which are stabilized by water-soluble gums and mucilages are still harder to break by a method which attempts to destroy the protective agent.

Many emulsions can be broken by the addition of another surface active agent. An agent which is more soluble in the dispersed phase will favor an emulsion with inverted phases and, if used in the right amount, will break the emulsion. Crude petroleum containing emulsified water is sometimes treated with soaps which are water soluble and also sufficiently soluble in the oil to enable them to diffuse through the oil to the water droplets. Sulfonated castor oil (Turkey-red oil) has frequently been used for this purpose.[8]

Foams are particularly susceptible to treatment with antagonistic surface active agents. Most foams that are met with in biochemical analyses can be broken by the application of capryl alcohol (secondary octyl alcohol) or related alcohols to the foam. A solution of the alcohol in water, or in a solution of a protein, will foam but, if an excess of the alcohol is present, droplets will be carried into the foam and cause it to break. A substance which will break a foam when applied to it is called a defoamer. An antifoamer prevents the formation of foam when present in solution. Some emulsions are called antifoamers although they are carried up into the foam as a separate phase where they function in the same way as a defoamer. The mechanism of defoaming is not well understood. Some emulsions produce copious foams but others are powerful antifoaming agents. Some foams may be broken by hot wires, jets of water, air, or superheated steam, or even by mechanical agitation. Agitation is frequently an effective method of breaking emulsions also. Cream emulsions are broken by churning with air to make butter, and numerous mechanical devices for breaking foams have been patented.

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[8] Monson, L. T., and Stenzel, R. W., *Alexander's Colloid Chemistry* **6**, 535 (1946).

Very dilute emulsions can usually be broken by filtering them through porous substances or by mixing them with powders which are preferentially wet by the dispersed phase. A dilute emulsion of water in an oil may sometimes be clarified by filtering through ordinary filter paper. The water droplets stick to the filter paper until it is saturated with water and will no longer pass oil.

Some emulsions can be broken by the application of electrical fields. Oil particles in water will move by electrophoresis, usually to the anode since organic acids and soaps are the impurities most likely to be present in oils. When high potential alternating currents are applied to W/O emulsions the drops of water line up in conducting chains. The high potential between adjacent drops then breaks down the protective layers in the oil between them and leads to coalescence of the drops.

There are a number of other ways of breaking emulsions. Freezing an emulsion forms ice crystals which rupture the protective films, and the emulsion may break when it is thawed. It is sometimes possible to dissolve both phases of the emulsion in a common solvent, but large quantities of the solvent will be required if the oil phase is a hydrocarbon.

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CHAPTER 11

HYDROUS OXIDES AND SILICATES

Coordination Shells of Water.—All ions in aqueous solutions are surrounded by water molecules which are held by ion-dipole attractive forces. Polyvalent ions have stronger attractive forces than monovalent ions and small ions have stronger forces than large ions. The size of an ion decreases as the number of electrons in the outermost shell increases and we find that the transition metals, such as Cr, Fe, and Cu, hold water and other polar substances very strongly. The bond between water and these elements, and also Al, is so strong that they form coordination compounds such as $Cu(H_2O)_4^{++}$ which may be represented as shown in Figure 11–1. The number of water molecules which can be attached in this way is determined by the coordination number of the ion. The coordination number may be either 2, 4 or 6, and depends, to some extent, on the size of the ion. Ag^+, and Cu^+ have coordination numbers of 2; Cu^{++}, Zn^{++}, Sn^{++}, and Hg^{++} and Si^{++++} usually have coordination numbers of 4; and Fe^{++}, Fe^{+++}, As^{+++}, Cr^{+++}, Sn^{++++}, Al^{+++}, and many others have 6 as a coordination number.

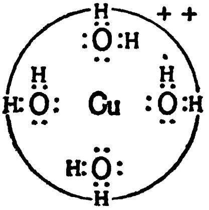

Fig. 11–1. The hydrated $Cu(H_2O)_4^{++}$ ion.

The water molecules in a coordination shell are held so strongly that the bonds between the oxygen atoms of the water and the metallic ion resemble covalent bonds, with two electrons from the oxygen atom holding the water to the ion. The oxygen atoms of the water are attracted so strongly that the bonds holding the hydrogen atoms are loosened and the hydrated ion is in fact acidic. The ionization of the hydrogen atoms attached to a ferric ion is shown in Figure 11–2. Only four of the six covalently bound water molecules are shown, the other two are to be imagined as located above and below the ferric ion.

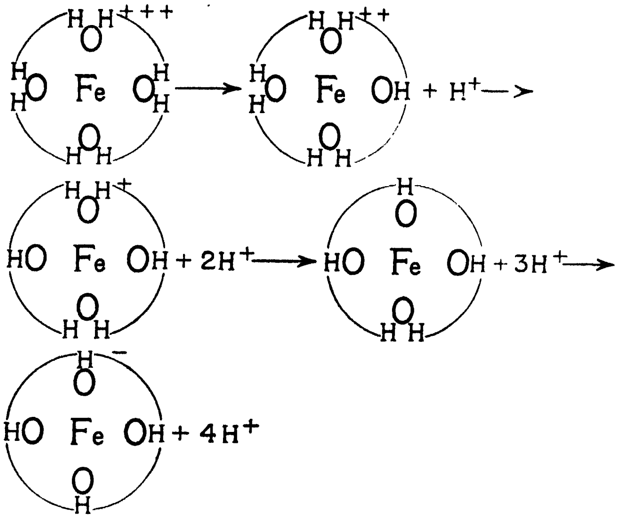

FIG. 11–2. Ionization of the hydrated $Fe(H_2O)_6^{+++}$ ion (only 4 of the 6 H_2O molecules are shown).

Solutions of ferric salts, such as ferric sulfate, are quite strongly acid because of the dissociation of the $Fe(H_2O)_6^{+++}$ ion to give $Fe(H_2O)_5(OH)^{++}$, H^+ and further dissociation products. The uncharged molecule $Fe(H_2O)_3(OH)_3$ is unstable and immediately polymerizes with loss of water as shown in Figure 11–3. The final product is α Fe_2O_3 (hematite) as a crystalline three-dimensional high polymer in which each Fe atom is joined to three O atoms, and each O atom is joined to two Fe atoms. When $FeCl_3$ is neutralized, the initial product is FeOOH $(\text{O—}\underset{\text{OH}}{\text{Fe}}\text{—O—}\underset{\text{OH}}{\text{Fe}}\text{—})$ which should be a linear polymer with a large number of —OH side groups. Hydrogen bonds between the chains would link them so tightly that the crystal would probably show none of the properties of a linear high polymer.

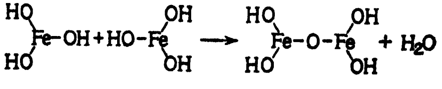

FIG. 11–3. Polymerization of $Fe(H_2O)_3(OH)_3$.

When an alkali is added to a dilute solution of Fe^{+++} ions a very large number of minute crystals of Fe_2O_3 are precipitated. The crystals which are formed on precipitation are so small that they do not give an X-ray diffraction pattern, but they do give an electron diffraction pattern corresponding to hematite. The interior of each particle therefore contains Fe and O atoms linked together by covalent bonds in a regular crystalline lattice. At the edge of the crystals the ferric ions will still have un-condensed —OH and OH_2 groups. The —OH groups can add H^+ ions and with them acquire positive charges. Figure 11–4a shows schematically a crystal of Fe_2O_3 with some attached H^+ ions on the surface of the crystal. In basic solutions some of the OH groups will dissociate to form OH^- ions which will be attached to the crystals. Figure 11–4b represents a crystal of Fe_2O_3 with attached OH^- ions.

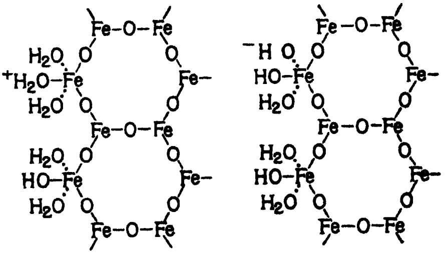

FIG. 11–4. Ionized $Fe_2O_3\,x\,H_2O$ particles.

The uptake of H^+ ions by Fe_2O_3 particles in acid solutions is frequently referred to as adsorption of hydrogen ions. This is a perfectly satisfactory interpretation of the facts, even though the hydrogen ions are attached by covalent chemical bonds to the rest of the crystal. When Fe_2O_3 particles are placed in basic solutions they acquire negative charges and this might be called adsorption of OH^- ions. However, what really happens is that the H^+ ions are lost and are neutralized by the OH^- ions in solution. The net result, so far as measurements go, is the same, for it is not possible to measure the number of water molecules attached to a colloidal particle in solution.

The insoluble hydroxides of most metals except the alkaline earths are qualitatively similar to ferric "hydroxide"; that is, they consist of crystals of colloidal dimensions which adsorb water and ions from solution. In some cases true hydroxides are formed with a composition corresponding to $Mg(OH)_2$ for example. In many other cases the crystal structure is that of an oxide and water is present only on the surfaces of the colloidal particles. The composition corresponds to an indefinite hydrate such as $Al_2O_3 \cdot x\, H_2O$.

It is ordinarily not possible to determine the structure from the composition of a colloidal precipitate, because a large fraction of the atoms will be at surfaces and adsorbed water and electrolytes will produce serious errors. X-ray examination of the precipitates can frequently establish the identity of the powder pattern with that of a known crystalline compound. Weiser and his students[1] have examined most of the inorganic colloids by X-rays and have identified the structure of the crystalline part of the precipitate.

The identification of a colloid as α Fe_2O_3, for example, means that Fe and O atoms are arranged in the α Fe_2O_3 crystalline structure within each particle. An oxygen atom at the edge of the crystal will have either an attached H atom or a negative charge. Some water will also be adsorbed in the available half of the coordination shell of the Fe atoms in the surface. The Fe and O atoms in the surface may be thought of as adsorbed ions, or they may be thought of as belonging to the crystal structure but having unsatisfied valence and coordination bonds which have reacted with the ions and molecules of the solution.

The Behavior of Colloidal Hydrous Oxides.—Two neutral colloidal particles of $Fe_2O_3\, x\, H_2O$ are very likely to stick together if they come in contact. Water will be eliminated between OH groups on the surface atoms of Fe, forming an oxygen bridge between the particles. If the particles touch at several points several oxygen bridges will be formed and the two particles will become one. If the solution is sufficiently concentrated, this process may continue until all the particles have stuck together. They will initially stick together only at the points of contact and will enmesh a large amount of water. The loose structure containing enmeshed solvent will be a gel. As the gel ages there will be some rearrangement of the atoms, and the crystal structure will become more perfect. Freshly precipitated ferric oxide gel is amorphous to X-rays but develops a hematite (α Fe_2O_3) structure as the gel ages. More dilute solutions of ferric "hydroxide" will form a flocculant precipitate.

If ferric hydroxide is precipitated in a slightly acid medium so that each particle carries excess positive charges (due to adsorbed H^+), the charges on one particle will repel the charges on other particles when they approach and there will be less chance that the particles will come in contact and stick together (see page 256). Since the positive charges keep the primary particles from sticking together and coagulating they are said to protect the sol. The primary particles of hydrated ferric oxide are of colloidal dimensions and if these particles are sufficiently protected by positive charges the colloidal sol will be stable.

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[1] See references at the end of this chapter.

There are several methods of preparing colloidal ferric oxide. Ferric chloride hydrolizes almost completely in boiling water to produce Fe_2O_3 and HCl. The HCl which is liberated may be removed by dialysis against distilled water to produce a stable brown colloidal sol. Each particle will have many positive charges and so there must be present in solution an equal number of negative ions, Cl^- in this case. There will also be a few H^+ ions produced by the further ionization of water molecules attached to peripheral Fe atoms. If all of the electrolytes are dialyzed out, the attached H^+ ions will also be lost and the sol will coagulate. It is therefore impossible to prepare a pure $Fe_2O_3\ x\ H_2O$ sol. In order that the sol be stable it is necessary to have some excess acid present; the H^+ ions on the sol particles and the anions as counter-ions in solution.

When a salt, such as NaCl, is added to a colloidal ferric oxide sol, the sol will coagulate. The presence of a large excess of Cl^- ions in solution means that there will be a Cl^- ion very close to every ⊕ ion on the surface of the colloid. These ⊖ ions will shield the ⊕ ions on the colloid and they will not exert a repulsive force on other positively charged particles. In other words the Cl^- ions reduce the stabilizing effect of the adsorbed H^+ ions and the sol coagulates.

Ferric oxide sols are coagulated by relatively small concentrations of sulfate ions. One ferric oxide sol was precipitated by 9 mM (0.009 molar) NaCl and by only 0.2 mM Na_2SO_4. The sulfate ion has two negative charges and it will be attracted more strongly to the positive charges on the particle than a chloride ion would be. As a result a much smaller quantity of sulfate ion will be able to shield the positive charges on the colloidal particles and cause coagulation.

The coagulating effect of other salts depends almost entirely upon the nature of the anion; that is, on the ion of opposite charge to the colloid. Potassium, sodium and magnesium sulfates are all good coagulating agents, and their chlorides are relatively poor coagulating agents. The only common anions of higher valence, which are stable in weakly acidic solutions, are the complex iron cyanide ions $Fe(CN)_6^{---}$ and $Fe(CN)_6^{----}$. As might be expected these ions cause coagulation when even more dilute than sulfate ions. Dye anions, such as the Eosinate ion, are usually strong coagulating agents even though they may be monovalent.

The Schulze-Hardy rule states that the coagulating or precipitating ability of an electrolyte increases with the valence of the ion of opposite charge to the charge on the colloid. As we have seen, sulfate ions are better precipitants than chloride ions for ferric oxide sols. Large organic ions, such as dyes and alkaloids, do not obey this rule. The precipitating ability of a monovalent dye anion, such as the Eosinate ion, is much greater than that of a chloride ion. A large organic ion is undoubtedly adsorbed on the surface of the colloidal particle by van der Waals' forces which help to hold the negative ion on the colloid where it completely neutralizes one positive ion. A chloride ion, in contrast, would be free to move around in the vicinity of the positive charge as a counter-ion. Therefore, several chloride ions would be required to shield each protecting positive charge on the colloidal particles.

The stability of a colloidal sol depends on the adhesive forces between particles and on the repulsive forces. The adhesive forces are low in the stable lyophilic colloids, which include many organic high polymers in good solvents. Thermal agitation is sufficient to keep these colloids in solution. Most mineral colloids have greater adhesive forces and are stable only if all the particles carry the same charge so that electrostatic repulsion will keep the particles separated.

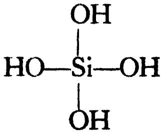
The stabilizing effect of ions on the surface of a colloid is determined by the number and effective range of the charges on its surface. Counter-ions which are strongly attracted to the charges on the surface will shield these charges and neutralize their repulsive effect on other charged particles. The electrophoretic mobility of a colloidal particle (or the zeta potential) also depends upon the number of charges on the particle and on the closeness of approach of the counter-ions. The electrophoretic mobility of a sol (or its zeta potential) is therefore closely related to its stability. You should not expect an exact equivalence between the electrophoretic mobility (which measures the charge density inside the layer of liquid that moves with an ion) and the coagulation (which depends on the effective electrostatic repulsion between the particles). Any given sol will coagulate when the zeta potential has been reduced to a certain limiting value. This value depends upon the type of sol and even upon the previous history of the sol but different ions will all cause coagulation at about the same zeta potential, or electrical mobility of the colloid. Different colloids will, however, coagulate at different zeta potentials.

A coagulated sol usually can be filtered but it will retain the coagulating ions as exchangeable counter-ions. If ferric "hydroxide" is precipitated in the presence of sulfate ions these ions will be carried down in acid solutions. If the solution is made basic with ammonia, enough hydrogen ions will dissociate to remove all the positive ions and produce some negative ions. The coagulated sol will bear negative charges and will carry positive counter-ions. Polyvalent counter-ions such as Mg^{++} will be adsorbed and carried down with the precipitate but sulfate ions can be quantitatively removed.

If a precipitate of positively charged $Fe_2O_3\,x\,H_2O$ is washed with water, the concentration of precipitating ions will be reduced and the sol may disperse again, or be peptized, and run through the filter paper. To avoid this, the analyst washes his precipitated "ferric hydroxide" with a solution of ammonium chloride. Some ammonium chloride is, of course, left in the precipitate but it volatilizes in the subsequent ashing and produces no error in the determination. Any ferric chloride which might be formed also hydrolizes in the presence of hot water to produce Fe_2O_3. When a precipitate of coagulated ferric oxide is dried, more water will be lost from OH groups on adjacent particles (forming oxygen bridges) and the coagulum will no longer be dispersible in water.

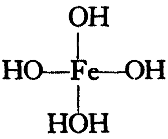
Many other metallic oxides are similar in most respects to ferric oxide. Examples include the hydrous oxides of zinc, copper, aluminum, chromium, manganese, titanium, cerium and the rare earths. There are, of course, quantitative differences in the behavior of these sols, some are more easily dispersed than others, but the over-all picture remains the same. They are all stabilized by the positive charges of "adsorbed hydrogen ions" which are attached to some of the peripheral OH groups forming H_2O molecules in the coordinating shell of the outside atoms.

Colloidal Silica and Silica Gel.—Silicon, in the silicate ion, is surrounded by a maximum of four oxygen atoms. The ortho silicate ion is SiO_4^{----}. Water glass contains a mixture of sodium silicates, including both the orthosilicate and the metasilicate, Na_2SiO_3 and probably higher silicates. When a solution of orthosilicate ions is neutralized, each oxygen adds a hydrogen ion to make the unstable orthosilicic acid:



$$\begin{array}{c} \mathrm{OH} \\ | \\ \mathrm{HO—Si—OH} \\ | \\ \mathrm{OH} \end{array}$$

Orthosilicic acid resembles ferric hydroxide,



$$\begin{array}{c} \mathrm{OH} \\ | \\ \mathrm{HO—Fe—OH} \\ | \\ \mathrm{HOH} \end{array}$$

and behaves in much the same way. Water is split out between pairs of silicon atoms leaving them linked by oxygen bridges. Orthosilicic acid polymerizes to form chains and cross-linked high polymers. The crystalline arrangement appears to be that of hydrous crystobalite, one of the crystalline modifications of SiO_2. In dilute solutions it is possible to prepare quite stable silica sols which are negatively charged. The anions responsible for the charge are the peripheral $\overset{\diagdown}{\underset{\diagup}{-\mathrm{Si}}}\mathrm{O}^-$ ions.

Silica sols have a great affinity for water and the shell of adsorbed water protects them from coalescence. It is possible to neutralize all of the negative charges and convert the sol to a positive sol by the addition of hydrogen ions without causing coagulation. This procedure is practical only with fairly dilute sols; much more concentrated sols can be prepared in alkaline solutions. Some authors maintain that ordinary water glass (which is manufactured by the action of water at high temperatures and pressures on a sodium silicate glass) consists of colloidal sodium silicate. The high viscosity of water glass supports the view that it consists of high polymers.

A concentrated solution of silicic acid sets rapidly to a gel. This gel, when dried to about 5% water, is the silica gel of commerce which is used as a dehydrating and adsorbing agent. Sodium silicate may be neutralized with ferric salts to produce a mixed precipitate of ferrix oxide and silica. (Ferric silicate is produced only at high temperatures in molten minerals.) The ferric oxide can subsequently be leached from the gel with acids, leaving a more porous structure.[2]

Silica gel, in common with many other gels, has the ability to contract and squeeze out spontaneously some of the water in the gel. This phenomenon is known as syneresis. Syneresis must be caused by a contraction of the units of the gel and is probably the result of the formation of additional bonds between different parts of the gel structure. Holmes found that the shrinkage of silica gels on drying could be reduced by first boiling the wet gel. Boiling water favors the dehydration of silica and produces additional bonds in the structure.

When silica gel is dried in air it shrinks because the tension of the water menisci in the capillary pores exceeds the tensile strength of the gel structure.

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[2] Holmes, H. N., and Anderson, J. A., *Ind. and Eng. Chem.* **17**, 280 (1925); and Holmes, H. N., Sullivan, R. W., and Metcalf, N. W., *ibid.* **18**, 386 (1926).

Kistler[3] has prepared a highly porous silica gel by a procedure which removes the solvent without forming an air-liquid meniscus. The gel, initially filled with water, is transferred to alcohol which diffuses in and replaces the water. The alcohol may then be replaced by a hydrocarbon, such as hexane, if desired. The gel still under the organic liquid is then heated in an autoclave under sufficient pressure to prevent the vaporization of the liquid. Heating is continued until the temperature rises above the critical temperature of the liquid. At this temperature the liquid becomes a gas and can be removed as such without the formation of a meniscus. The dry "aerogel" is highly porous and will collapse if it is wet with water or alcohol and then allowed to dry.

Quartz is a crystalline form of silica which may be regarded as a completely cross-linked high polymer. Each silicon atom is attached to four oxygen atoms and each oxygen joins two silicon atoms. The silicon has an effective charge of $+4$ and the oxygen -2. The silicate minerals contain other metallic oxides which replace some of the silica. There are two types of metallic substituants which may occur in a silicate mineral. Atoms such as aluminum and iron, the R_2O_3 elements, will replace silicon atoms in the lattice. Each Al atom will be surrounded by four oxygen atoms and there will be an excess of negative charges due to the extra oxygen atom. This pair of negative charges can be satisfied by a single Ca^{++} or Mg^{++} ion or by a pair of K^+ or Na^+ ions. These ions are outside the main lattice structure and may be exchanged for other ions if there is room for the ions to get in and out.

Silicate minerals have many of the properties of completely crystallized high polymers. Some minerals, such as quartz, exist as a three-dimensional cross-linked polymer. Every atom inside a crystal of quartz is linked to every other atom by essentially covalent bonds. Some silicate minerals exist as two dimensional sheets—for example, the micas and talc. Strictly linear high polymeric silicates are not known but the asbestos minerals consist of narrow ribbons only a few atoms wide. The individual planes of a sheet mineral, such as mica, are held together by relatively weak van der Waals' forces and the mineral is easily split into thin layers.

Glass consists of silicate high polymers which have not had time to crystallize in cooling. If a molten silicate is cooled rapidly the atoms will not be able to adjust themselves to a crystalline arrangement and the cooled material will be amorphous like a liquid. The interatomic bonds will be too strong to allow the individual atoms to change their positions and the glass will therefore be rigid.

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[3] Kistler, S. S., *J. Phys. Chem.* **36**, 52 (1932); see also Mantell, C. L., *Adsorption*, pp. 167–172 (1945).

Silica itself becomes a glass if it is cooled rapidly from the molten condition. Each silicon atom in fused silica (incorrectly called fused quartz) will be attached to four other silicon atoms by oxygen bridges but there will be no over-all regularity. Figure 11–5a represents a regular crystalline arrangement of silicon-oxygen bonds (only three bonds are shown for each silicon atom; the fourth may be imagined as extending above or below the plane of the diagram). Figure 11–5b shows the arrangement of the atoms in a glassy or amorphous structure. Each silicon atom is still bonded to four divalent oxygen atoms but there is no regularity on a larger scale. Much the same sort of structure exists in ordinary glass except that some of the silicon has been replaced by other metals, such as Na and Ca.[4]

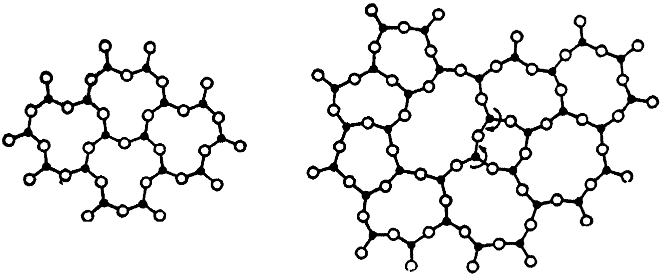

Fig. 11–5. Two-dimensional representations of (a) crystalline and (b) glassy SiO_2 structures (only 3 of the 4 bonds on each Si atom are shown). (From Huggins et al., *Alexander's Colloid Chemistry* 5, Reinhold (1944).)

The sodium ions in glass are readily soluble in water but the structure of glass is such that it is relatively difficult for the sodium ions to escape. If glass is ground under water, enough alkali will be liberated to color phenolphthalein pink. The surfaces of glass vessels that have been exposed to moisture consist of a highly porous silica structure which may be as thick as 1000 Å. This highly porous surface accounts for the great adsorptive capacity of glass. Surprisingly large amounts of a dye, such as methylene blue, will be adsorbed on the surface of a used flask and can be removed only by washing with an organic solvent which contains exchangeable cations, such as glacial acetic acid or alcoholic HCl.

The zeolites are silicate minerals which have a highly porous three-dimensional structure. This structure is represented in Figure 11–6 which shows the cage-like structure of the individual units of the crystal. The pores are large enough to permit water and small ions to penetrate. The zeolites contain alkali ions which are held in the structure by electrostatic attraction to —O⁻ ions. When a zeolite mineral is filled with water the alkali ions can exchange for other cations; for example, two Na^+ ions may exchange for one Ca^{++} ion in the water softening process. Exchange on zeolytes takes place primarily within the pores, and large organic cations, such as the tetraethyl ammonium ion, $N(C_2H_5)_4^+$, are too large to enter the pores and will not be exchanged.

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[4] See Weyl, A. W., *J. Applied Physics* 17, 628 (1946).

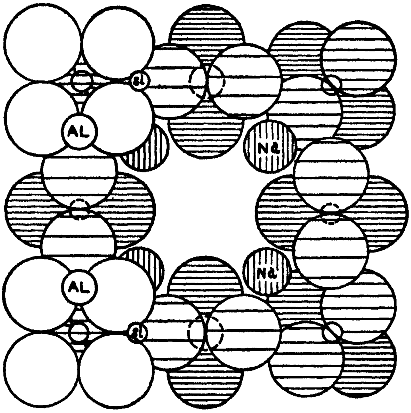

FIG. 11–6. Diagram of the structure of a zeolite mineral according to Jaeger. (Redrawn from H. Jenny, *J. Phys. Chem.* **36** (1932).)

Soil Minerals.—The colloidal soil minerals of greatest importance are the clays. Clays consist of one or more of a series of plate-like silicate minerals which are highly hydrated. The clay minerals are formed by the action of water and weak acids, primarily H_2CO_3, on the silicate minerals of rocks such as feldspar. Hydrogen ions replace alkali, and alkaline earth ions in the rock minerals and the resulting —OH groups attract more water. The —OH groups are essentially chemically combined water since they will combine by pairs and split out water when the clay is heated strongly.

Clay minerals are made up of successive layers of silicon oxides and aluminum oxides. (Some Al may be replaced by Fe.) Some of the oxygen atoms of the silicon oxide layer are also members of the aluminum oxide layer and serve to bind the two layers together.

Since there are not enough valences on the aluminum atoms to balance all of the valences of the oxygen, the excess oxygen valences will be satisfied with hydrogen as hydroxyl groups. Figure 11–7 shows the probable structure of montmorillonite, a clay mineral found in bentonite. It should be noted that the atoms are drawn too small in relation to their spacing. The oxygen atoms should be large enough to touch each other and the other atoms should be enlarged proportionately. Figure 11–8 is a photograph of a model representing the location of the atomic centers in montmorillonite.

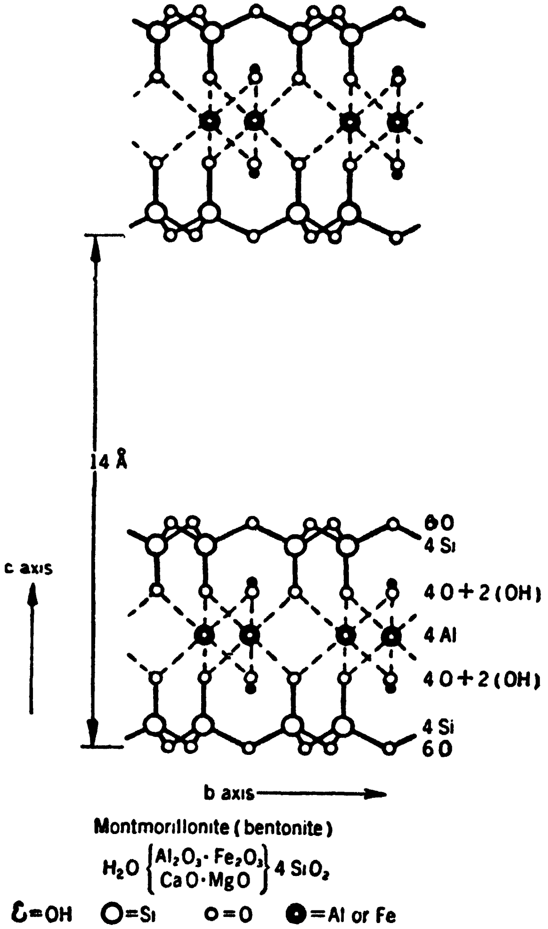

FIG. 11–7. Structural diagram of montmorillonite. (From Meyer, *High Polymers* 4, Interscience (1942).)

When montmorillonite has the structure shown in Figure 11–7 hydrogen atoms occupy all of the available base exchange positions. Some of the hydrogen on the —OH groups can ionize leaving minus charges on the mineral. These charges will hold exchangeable cations. Most clays in the soil have a large fraction of their exchangeable hydrogen replaced by other cations, especially K^+ and Ca^+.

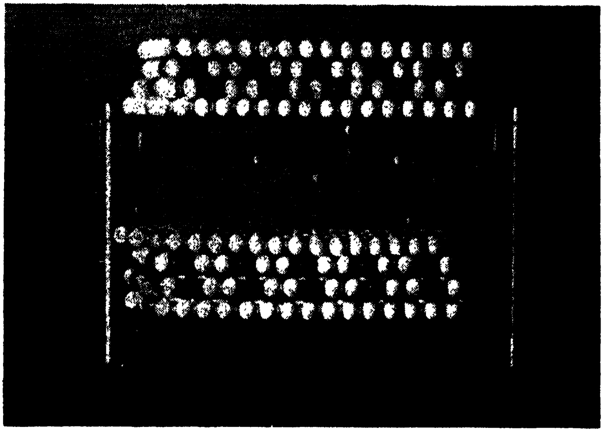

FIG. 11–8. Montmorillonite. (*Courtesy of C. E. Marshall.*)

Nearly all of the K^+ and Ca^{++} ions in a soil are bound to the colloidal material. The concentration of salts in an aqueous soil extract is usually too low to permit plant growth. Plants which do grow in the soil must therefore utilize the exchangeable ions on the soil colloids. The root hairs of the plants come in contact with the soil colloids and are able to remove cations by direct exchange for hydrogen ions supplied by the root. The soil colloids include organic matter as well as clay minerals but relatively little work has been done on the properties of the organic substances in the soil. These should provide a fruitful field for research.

All clay minerals adsorb water strongly. The montmorillonite group, which includes the bentonite clays, takes up water in the layers between the silicon-oxygen sheets. In this respect its behavior resembles that of strong soap solutions which can take up both water and oils in layers between the soap micelles (see Figure 9–18). The interplanar water of a bentonite clay is held reversibly and may be removed by drying, and replaced by wetting the clay. Kaolinite, or china clay, minerals do not have an expanding lattice and take up water very slowly once they have been air dried. When clays are heated above 400° C. they lose water of constitution—that is, water present as —OH groups. The loss of this water breaks up the structure of the mineral. When clay articles, such as bricks or pottery, are fired, the water of constitution is lost and some of the lower melting minerals fuse and stick the remaining particles together. The loss of water produces a porous structure and the articles shrink. Excessive shrinkage can be prevented by incorporating minerals of high silica content which have a high melting point. When acid washed clays are heated to very high temperatures the alumina and silica separate as individual minerals. This forms the basis for most attempts to recover aluminum from ordinary clays.

The outstanding physical property of clay-water systems is their plasticity. Clays consist of small plate-like particles which may be as great as 20,000 Å (2μ) wide and as little as 10 Å thick. These thin sheets are covered with water which is adsorbed by van der Waals' forces on the exposed oxygen and hydroxyl layers. The adsorbed water on the flat sheets keeps them separated, but there may still be attractive forces between the edges of the sheets where the crystal structure has been interrupted and there are "broken" bonds (satisfied by —OH groups or $—O^-$ ions).

The adsorbed water on the flat sheets will hold the individual particles apart with a relatively weak force. This repulsion will be augmented by the ionic repulsion between like charges on the clay particles. Sodium counter-ions, for example, do not approach very close to the particles and have a relatively small shielding effect. The addition of neutral salts, such as NaCl, will eventually crowd in the counter-ions until the electrostatic forces are no longer sufficient to hold the particles apart, and the clay will coagulate. Calcium ions are much more effective in causing coagulation and, as might be expected, trivalent ions are even more effective. (Magnesium ions are reported to behave more like Na^+ ions than Ca^{++} ions. They are probably very highly hydrated.) The addition of sodium hydroxide disperses clays by replacing bound hydrogen with ionized Na^+ ions.

An ideal soil consists of clay particles which are partially saturated with Ca^{++} ions and contain some exchangeable K^+ ions. If the plants remove too many K^+ ions replacing them with H^+, the soil will become acid and it will be harder for the plant to obtain nutrients. If too much Na^+ is present, the clay particles will disperse and fill up the capillary spaces between the granules. This will greatly reduce the water permeability of the soil and make it unsuitable for agricultural purposes. The dispersing action of sodium salts on clays has been used to make earth dams and ponds watertight. A noteworthy example was the lagoon at Treasure Island in the Golden Gate World's Fair of 1939–1940. The lagoon had a clay bottom and initially leaked at a rate of 1 inch per day. This was remedied by filling the lagoon with sea water. The sodium ions in the sea water dispersed the clay so that the fine particles filled up the capillary spaces. When fresh water was replaced in the lagoon the drainage rate had been reduced to 0.1 inch per day.[5]

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[5] Lee, C. H., *Proc.*, *ASCE*, p. 247 (1940).

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CHAPTER 12

LYOPHOBIC COLLOIDS OR SUSPENSOIDS

Stabilization.—The lyophobic colloids are a class of colloidal suspensions which are inherently unstable and will eventually coagulate. If a lyophobic colloid is precipitated or coagulated it is usually very difficult if not impossible to redisperse it. Lyophobic colloids are frequently called suspensoids, and in aqueous systems the term hydrophobic may be used.

Most inorganic colloids can be classified as suspensoids. Some organic systems, such as very dilute oil in water emulsions, also behave like suspensoids. The stable colloidal sols have already been discussed. These were originally called emulsoids or lyophilic systems. Most stable colloidal suspensions are either organic high polymers or colloidal electrolytes, although many of the hydrous oxides and silicates are hydrophilic systems.

Early workers with colloidal systems strove to make pure colloids, such as a colloidal gold sol containing only gold and water. However, it is difficult to remove all the impurities because colloidal systems have great adsorptive capacities. Most of the early preparations contained unidentified constituents which acted as stabilizing agents. Those workers who did succeed in removing the impurities nearly always produced unstable systems.

It gradually became apparent that colloidal suspensions of substances which have little affinity for the solvent will be unstable unless some stabilizing agent is present on the interface. Two types of stabilization are possible. A protective colloid, which is always an inherently stable colloid, may be adsorbed on the surface of the lyophobic particles. The surface of the particles will then have the properties of the stable colloid, and as a result the system will be stable. Most stabilized emulsions are of this type. Dispersed particles will also be stable if there is a repulsive force between the particles which keeps them from coming in contact. The only repulsive force which is sufficiently strong is the force between like electrical charges. Lyophilic colloids usually carry ions and show electrokinetic properties.

Colloidal sols which are stabilized by ionic repulsion will usually be only temporarily stable or lyophobic. The repulsive forces between like charges may be sufficient to prevent the collision of two particles which have the average kinetic energy. But in any solution some units have more energy than the average and some have less. There will always be a few particles which have even as much as twenty times the average kinetic energy.

The probability that a particle will have twenty times the average kinetic energy is

$$20e^{-(3/2)^{20}} \quad \text{or about } 2 \times 10^{-12}.$$

This is a very small probability but it becomes large when multiplied by the number of molecules in a mol.

If the repulsive forces are sufficient to prevent the collision of particles which have twenty or more times the average kinetic energy the sol will be relatively stable. Only a few particles will ever actually collide and stick together and it may take centuries to produce coagulation. Some of Faraday's original gold sols which were prepared in 1857 are still in suspension. Only a small fraction of the gold has coagulated as a black sediment.

The Size of Crystals.—Nearly all insoluble precipitates exist in a crystalline form. Many which were thought to be amorphous because they did not show X-ray diffraction rings have been found to be crystalline when examined by electron diffraction. When a crystal is formed in a solution it is necessary for the molecules to arrange themselves in a definite geometrical pattern. Very few substances will form new crystals when their solutions are barely saturated; it is usually necessary to make the solution super-saturated to some degree before crystals will form. If crystal nuclei are present, crystallization will take place in saturated solutions. The best nuclei are crystals of the substance being crystallized. Solid particles which have the same or nearly the same crystal structure will also serve as crystallization nuclei and reduce the required degree of supersaturation.

There is no fundamental difference between the supersaturation of a solution and the undercooling of a pure liquid below its melting point. Water can readily be undercooled 5° or 6° C. before it will crystallize. The extent of undercooling can be reduced to less than 1° C. by the introduction of crystals of beryl (berylium aluminum silicate) which crystallizes in the same system as water.

The degree of supersaturation which a liquid will maintain without the formation of crystals is a function of the time of observation. The formation of a crystal nucleus requires the simultaneous presence of a number of molecules all having reduced energies. Obviously the longer one waits, the better chance there will be that a crystal will be formed.

The chance of forming crystal nuclei will be zero in a saturated solution and will not be appreciable until the concentration is quite a bit greater than saturated. The rate of growth of a crystal will, however, be proportional to the absolute supersaturation, $c - c_s$, where c is the concentration and c_s is the concentration of a saturated solution. If c is only slightly greater than c_s the formation of nuclei will be extremely slow and each nucleus will grow to a relatively large crystal. As the concentration is increased the number of nuclei formed will increase more rapidly than the concentration and the resultant crystals will be smaller because all of the substance will have crystallized before the crystals grow large.

In order to obtain particles of colloidal dimensions it is necessary to work with relatively concentrated solutions or with substances which are very insoluble. The rate of growth of a crystal is proportional to the absolute supersaturation $c - c_s$ but the rate of formation of nuclei is a function of the relative supersaturation $(c - c_s)/c_s$. If we reduce the solubility of a substance by changing the medium we will increase the relative supersaturation more than the absolute supersaturation and therefore increase the number of particles and decrease their size.

Sodium chloride crystallizes from water in large crystals because it is impossible to produce large values of the relative supersaturation. If sodium chloride is produced by the interaction of sodium ethylate and hydrochloric acid in an organic solvent (such as ether and amyl alcohol) in which the sodium chloride is practically insoluble, the precipitate consists of crystals of colloidal dimensions. To obtain a precipitate of colloidal dimensions we should combine the reactants in as concentrated a solution as possible and in a solvent in which the precipitate will be the least soluble. (Although concentrated solutions favor the formation of small particles the particles may touch and form a gel, or precipitate as a curd, if the absolute concentration is high.)

It is very difficult to maintain a suspensoid sol in a medium in which the substance is appreciably soluble. The process of solution and crystallization in a saturated solution is dynamic and any crystal is continuously gaining and losing molecules. This process makes very little difference to large crystals but leads to the disappearance of very small crystals by a purely statistical process. If a small crystal randomly gains and loses molecules for a long enough time there is a chance that it may lose all of its molecules. If this happens the crystal of course ceases to exist and the average size of the other crystals will be increased. The smaller a crystal is, the greater is the probability that it will dissolve completely. If half of the crystals disappear the average volume of the remaining crystals will be doubled.

A crystal has a good chance of losing all of its molecules if the number of molecules in the crystal is equal to or less than the square root of the number of fluctuations, which in this case is the number of times a molecule is added to or removed from the crystal. The rate of movement of liquid molecules from one "hole" to another is about 10^9 per second. In one day there are 86,400 or about 10^5 seconds. The maximum number of fluctuations per day is therefore about 10^{14}. Since not all molecular displacements will be effective we can take 10^{12} as a more probable value of the number of times a molecule is added to or removed from a crystal. It will of course be less if the substance is very insoluble. If the crystal contains 10^6 molecules and gains and loses 10^{12} molecules in a completely random manner it has a good chance of disappearing. A cubic crystal which contains 10^6 molecules will have 100 molecules on a side and will be a few hundred Å in diameter.

The growth of the larger crystals in a precipitate at the expense of the smaller ones is frequently made use of in analytical chemistry. Fine-grained precipitates may be left to digest on a steam bath overnight so that they will filter more easily. The use of a steam bath increases the solubility and favors the process of solution. Many micro-crystalline precipitates are also cemented together into larger aggregates during digestion and this process accounts for much of the improvement in the filterability of the precipitate.

Small liquid drops with curved surfaces are more soluble than large drops for another reason. The surface tension produces a pressure in the drop which squeezes molecules out into the solution. The smaller the drop the greater will be the pressure and the greater the solubility. The effect of droplet size on the solubility of the dispersed phase is negligible for droplets greater than 0.1μ in diameter. Although the surface of a crystal is flat its surface energy is proportional to its area, and in a given quantity of suspension the surface energy is inversely proportional to the diameter of the particles. Any process which decreases the surface energy will be a spontaneous process and therefore small crystals will tend to dissolve and crystallize on the larger ones. The surface tension of a solid is very hard to define. It would be expected to vary from molecule to molecule over the surface of a crystal, and there are probably no accurate measurements of the surface tension of solids.

The fact that small crystals disappear and recrystallize on larger crystals when a slightly soluble precipitate is aged has usually been explained as the result of surface tension forces on the smaller crystals making them more soluble. The phenomenon is called "Ostwald Ripening." Many attempts have been made to measure the increase in the solubility of small crystals. Most of the measurements are open to question for a number of reasons. Attempts to measure the concentration by the electrical conductivity of the sol neglect the conductivity of the adsorbed ions near the surface of the particles. Measurements on finely ground crystals would be likely to be in error because grinding exposes unstable and more soluble faces to the solution. The calculated values of the surface tension based on these measurements may be completely unreliable.

Methods for Preparing Suspensoids.—Nearly all of the practical methods for preparing suspensoids produce the particles by the aggregation of molecules. It is very difficult to grind particles of a powder much finer than 0.1μ in diameter. When particles are reduced to this size it is impossible to apply enough force to split them because the powder particles cushion the blow of any crushing device and prevent its further action. So-called colloid mills are effective machines for dispersing coagulated colloids whose individual particles are stuck together by relatively weak bonds, but they are unable to reduce a crystal to a colloidal suspension. Some colloidal particles may be formed when heavy blows, such as are produced by explosions, are struck on massive materials, but only a minute fraction of the total mass is reduced to colloidal dimensions.

Colloidal salts are usually produced by double decomposition. If the solutions containing the component ions of an insoluble substance are mixed, a precipitate will form. If the substance has a low enough solubility the precipitate will be colloidal. For example, we can mix silver nitrate and sodium iodide and obtain a colloidal precipitate of silver iodide.

$$(Ag^+ + NO_3^-) + (Na^+ + I^-) \longrightarrow AgI \downarrow + (Na^+ + NO_3^-).$$

The colloidal precipitate will be left in solution with the counter-ions of the two salts and the precipitating ion which happens to be in excess. It is impossible to mix exactly equal numbers of Ag^+ and I^- ions, because even one drop (0.05 ml) of a 0.001 N solution contains 3×10^{16} ions, and either Ag^+ or I^- ions are sure to be present in excess. The counter-ions, which are left over when the precipitate forms, frequently reduce the stability of the particles and produce coagulation. The coagulating effect can be reduced by choosing monovalent counter-ions and working in as dilute a solution as possible. Some reagents react in such a way that there are no ionized products. For example, barium sulfate can be formed by the action of sulfuric acid on barium hydroxide; water is the only other product. Likewise, if H_2S is used to precipitate HgS from a solution of $Hg(CN)_2$, the counter-ions will combine to form HCN which is almost un-ionized.

The hydrous oxides and hydroxides are frequently formed by hydrolysis. These hydrated ions are fairly strong acids and lose hydrogen ions in dilute solutions with the formation of the insoluble hydroxide (see Chapter 11). The hydrolysis of ferric chloride is almost complete in dilute boiling solutions. A very stable sol of hydrous ferric oxide can be made by boiling a dilute solution of ferric acetate until all the acetic acid has evaporated. This usually takes several days and the water must be continuously replaced.

Organic esters of silicon, such as ethyl silicate, will hydrolyze in water to produce colloidal silicic acid, $Si(OH)_4$, and alcohol but no counter-ions. Silicon chloride will also hydrolyze in water, but it leaves HCl in solution. Very pure sols of the hydrous oxides can be prepared by passing a solution of the salt through an ion exchange column. Stable silica sols, for example, can be prepared by passing dilute sodium silicate through a cation exchange column which is saturated with hydrogen ions. This sol may be stabilized by adding a trace of alkali or some of the sodium silicate solution. Acid exchange resins might also be used to prepare sols of the metallic oxides such as Fe_2O_3. Surprisingly the sols do not gel in the column and clog it up.[1]

Colloidal Metals.—Colloidal suspensions of elements are usually produced by the reduction of their ions. Metals are extremely insoluble in all nonmetallic solvents and, therefore, when metallic ions are reduced in an aqueous system they must produce a colloidal suspension if nuclei can form. Some systems contain very few nuclei and the metal comes out of solution on the surface of the vessel as a mirror. This is the usual result when silver ions are reduced by organic reagents in a clean glass vessel.

A mirror consists of colloidal particles which are in contact with one another. There is no over-all crystalline structure in the mirror although a thick mirror may build up crystals on its exposed surface.

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[1] Ryznar, J. W., *Ind. and Eng. Chem.* 36, 821 (1944); and *Alexander's Colloid Chemistry* 6, 1113 (1946).

The structure of the surface of a mirror on glass closely resembles the structure of a polished metal surface. Polishing deforms the crystals on the surface until they form an amorphous layer. The structure is therefore more like a liquid than a macroscopic solid.

Gold ions can be reduced by almost any reducing agent to form colloidal gold. The Au^{+++} ion is not stable as such, but exists in solution as a complex ion. Gold chloride probably contains some $Au(Cl_6)^{\equiv}$, and chlorauric acid contains the $AuCl_4^-$ ion. Gold may also exist as the aurate ion, $Au(OH)_4^-$. When a solution of gold chloride is neutralized by potassium carbonate and treated with formaldehyde, a red sol of colloidal gold will be produced. Assuming that potassium carbonate converts the auric ion to the aurate ion we can write the reduction in two half reactions.

$$2\,Au(OH)_4^- + 6\,e^- \longrightarrow 2\,Au\downarrow + 8\,OH^-$$

$$3\,H_2CO + 9\,OH^- \longrightarrow 3\,HCOO^- + 6\,H_2O + 6\,e^-.$$

The gold is formed as a highly supersaturated solution which condenses to a colloidal sol.

If special precautions are taken to clean the apparatus and if water distilled in an all glass still is used, the gold sol will be red in color. This is a very unstable sol and very small traces of polyvalent cations will coagulate it to a blue sol. Larger concentrations will produce a black precipitate. The stabilizing charge on the gold particles may be $\overset{\diagdown}{\underset{\diagup}{—}}\mathrm{AuOH}^-$ ions or $\overset{\diagdown}{\underset{\diagup}{—}}\mathrm{AuCl}^-$ ions.

At least 65 different reducing agents have been used to prepare sols of colloidal gold and the number of possible agents is undoubtedly much greater. A good red gold sol can be prepared by reducing a neutralized solution of gold chloride with a solution of ascorbic acid. Vitamin C pills, which may contain a colloidal binder as well as ascorbic acid, produce quite stable red gold sols.

It is difficult to prepare stable red gold sols which do not contain some stable colloidal (emulsoid) as a stabilizing agent. Very stable red gold sols can be prepared even in tap water by the use of tannin as a reducing agent. Tannin is a high molecular weight glucoside containing many phenolic groups. It acts as a reducing agent and the colloidal particles become covered with a layer of tannin. Many of the properties of this sol are the properties of tannin and not the properties of the gold.

In order to obtain a good red gold sol it is necessary to have nuclei present for the gold to form on. Some reducing agents, especially a solution of phosphorous in ether such as was used by Faraday in 1857, favor the spontaneous formation of nuclei. Thiocyanates also form many nuclei. Other reducing agents, such as hydroxylamine, H_2NOH, inhibit the formation of nuclei and usually produce blue sols with large particles. An agent which reduces the rate of growth of the nuclei by adsorbing on the surface, such as tannin, will also produce a red sol but the formation will be much slower.

A homogeneous gold sol can be prepared by adding a sol which contains very small particles to gold ions and a reducing agent which inhibits nuclei formation such as hydroxylamine. The particles of the added sol act as nuclei and they all grow at the same rate until the gold ions are exhausted. The particles of some gold sols are too small to be visible in the ultramicroscope, but they can be enlarged by using them as nuclei for the deposition of more gold until they are large enough to be counted. The smallest particles of gold which are ordinarily visible in the ultramicroscope are about 60 Å in diameter. Nuclear gold sols have been prepared which are as small as 26 Å in diameter. It is claimed that particles as small as 18 Å on a side have been "measured" by the breadth of the X-ray lines.[2]

Colloidal silver can be prepared by the same methods which are used to prepare colloidal gold. Nuclei are less likely to form spontaneously and, in clean glassware, silver which is reduced by an aldehyde comes out as a mirror. If the glass is covered with a layer of oil or grease it is possible to get a grey sol of colloidal silver. Unprotected silver sols are not very stable because of the solubility of silver oxide and the relative ease of oxidation of the silver.

Many colloidal silver preparations are used in medicine. These are all stabilized by protective colloids. Argyrol, for example, is a colloidal silver sol which is protected by the protein vitellin, from egg yolks. There are several other silver sols which may be used in the same way. All colloidal silver preparations serve as a source of silver ions which are liberated slowly. Silver ions are toxic to all living cells but are especially toxic to one-celled organisms such as bacteria. Larger organisms can precipitate the silver ions in their outer layers and survive the treatment.

Plastic trays and other articles containing colloidal silver have been developed which can be used as a continuously sterile surface. A surgeon can leave sterile articles on this surface without fear of contamination. Metallic silver also gives off silver ions, and sometimes also colloidal silver. Enough Ag^+ ions are liberated to sterilize liquids which remain in contact with the metal. A silver communion cup which is used by a large number of people can be more sanitary than individual glasses which have been rinsed in warm water and dried by hand on a towel.

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[2] Scherrer, P., and Staub, H., *Z. physik Chem.* **A 154,** 309 (1931); *Helv. Phys. Acta* **3,** 457 (1930). See also Weiser, H. B., *The Colloidal Elements*, p. 59 (1933).

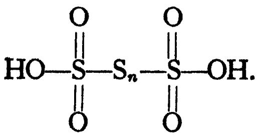
Colloidal sols of the platinum metals behave in most respects like gold sols. Sols of most other metals are unstable because of oxidation and the solubility of the ions. Many metals can be obtained in a colloidal state by rapid electrolysis of solutions of their simple ions. Electrolysis can be regarded as direct reduction by electrons. The colloidal metal frequently sticks to the cathode as a porous deposit, but may come off as an unstable sol. Platinum black for electrodes is prepared by the electrolysis of platinum chloride on a gold or platinum electrode.

Colloidal metallic deposits are ordinarily not desired by electroplaters; they demand bright mirror-like deposits. Bright deposits can most easily be obtained by electrolyzing solutions which contain complex ions, especially the cyanides. A complex ion holds most of the metal in the form of an anion but maintains a very dilute concentration of the free cations. When electroplating is done from extremely dilute solutions of the cations (maintained by dissociation of the complex anions) the atoms deposit in a coherent layer which has many of the properties of a mirror. Electroplated surfaces usually contain many "pinholes" which can be removed by burnishing. Some of these holes probably correspond to other positively charged suspended matter in the plating bath which is deposited on the cathode with the metal. The Tyndall cone is sometimes used to examine plating baths for the presence of suspended matter.[3]

Colloidal sulfur can be prepared by a variety of different reactions. The most stable sulfur sols can be prepared by the reaction of concentrated solutions of SO_2 and H_2S. The reaction may be written:

$$2\,H_2S + SO_2 \longrightarrow 3\,S\downarrow + 2\,H_2O$$

but other reactions also occur. This colloidal sulfur contains thionic acids with the formula



$$HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-S_n-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-OH.$$

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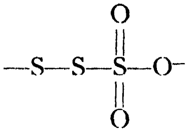
[3] See Weisberg, L., *Alexander's Colloid Chemistry* **6**, 579 (1946).

It is probable that the sulfur particles also contain attached sulfonate ions



$$-S-S-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O^-$$

corresponding to thionic acids with very high values of *n*. This sol has been studied by Odén who found that it was so stable[4] that it could be precipitated by salt, filtered and completely redispersed in fresh water. This sol is thus a lyophilic colloid and resembles a protein solution. Odén also found that the larger particles were less stable and would coagulate upon the addition of a solution of NaCl too dilute to coagulate the finer particles. In this way he was able to fractionate the sol and obtain a series of sols with nearly uniform particle diameters.

Colloidal sulfur can be prepared by decomposing thiosulfates, and polysulfides with acids. The stable sols formed by the decomposition of thiosulfates are probably also stabilized by attached sulfonate ions.

An unstable sulfur sol can be prepared by pouring an alcoholic solution of sulfur into a large volume of water. The sulfur is molecularly dispersed in the alcoholic solution but is insoluble in a dilute solution of alcohol in water. This sol is unprotected and coagulates in a few hours, depositing a white precipitate of sulfur. It could be stabilized by pouring the solution of sulfur into a solution of a water-soluble stabilizing colloid. Most solids and liquids which are insoluble in water but soluble in alcohol or dioxane (which will mix with all liquids between water and the paraffins) can be brought into colloidal dispersion in this way. A sol, or emulsion, prepared by the displacement of a good solvent is ordinarily unstable. It can usually be stabilized by a soap or other hydrophilic colloid. The author once prepared colloidal phenolphthalein in this way using alcoholic solutions and a number of different detergents as stabilizing agents. Some of the sols were stable for periods up to one month but all eventually settled out. Phenolphthalein is soluble to the extent of 0.18 g per liter and this solubility led to growth of the large crystals at the expense of the smaller ones until the crystal size exceeded the colloidal range and the crystals settled out of solution.

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[4] See Svedberg, T., *Colloid Chemistry*, 2nd Ed., p. 66 (1928).

Another method of preparing colloidal sols, which is essentially similar to that just described, is by the condensation of vapors in the liquid phase. Emulsions are formed in this way when aniline is steam-distilled. An unstable emulsion of mercury can be produced by passing mercury vapors into water. Sulfur sols can also be prepared in the same way.

One very convenient way of producing the vapor of a metal is to strike an arc between two electrodes of the metal under a liquid. This method was discovered by Bredig in 1898 and has been greatly improved by Svedberg.[5] Colloidal sols prepared by Bredig's method are hetero-disperse and usually contain a large amount of oxidized metal. Svedberg found that sols could be formed by enclosing the arc in a quartz tube and blowing the vapors with nitrogen through a hole in the tube into the surrounding liquid. In this way he was able to prepare colloidal sols of nearly all metals. Many metals which react with water can be prepared as sols in organic liquids (this is not practical with the exposed direct current arc because the heat of the arc decomposes the liquid). Svedberg also used a very high frequency arc with which he was able to obtain sols of even very reactive metals, such as sodium, in ether.

Sols produced by Bredig's method are unstable unless suitable agents are added to the water. Most of the metals form oxides and these can be ionized by acids or bases. Colloidal lead, for example, can be stabilized if alkali is added to the water surrounding the lead electrodes. This probably produces some attached plumbite ions, $—PbO^-$, on the particles.

Purification of Sols.—Most methods for the preparation of the lyophobic colloids leave electrolytes in solution. For example, colloidal gold contains K^+, Cl^-, HCO_3^-, $CO_3^=$ and $HCOO^-$ ions; colloidal silica contains Na^+ and Cl^- ions. In many cases these ions must be removed or they will slowly coagulate the sol. Excess ions can be removed by filtering a coagulated sol but as soon as the coagulating ions are removed the sol will disperse and run through the filter paper.

The most practical method for removing electrolytes from a sol is that invented by Graham, and called by him dialysis (see Chapter 2). The sol is placed in a membrane, such as a Visking sack, which has pores large enough to pass small molecules but not colloidal particles. The sack is suspended in running water until all the small molecules have dialyzed out.

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[5] See Svedberg, T., *Colloid Chemistry*, 2nd Ed. pp. 39–51 (1928).

The size of the pores is not the only factor which determines whether a particle will be able to get through a given membrane. If the particle is strongly adsorbed on the pore, it may clog the pore and prevent other particles from getting through. Membranes which have attached ions are therefore usually impermeable to particles bearing the opposite charge. Some membranes appear to sorb water very strongly and negatively sorb substances in solution. It has been claimed that the pores of copper ferrocyanide membranes are much larger than sugar molecules but that sugar is negatively sorbed and cannot get close to the walls or into the pores.[6]

The removal of electrolytes by dialysis frequently disperses or peptizes a sol which has been coagulated by salts. A stable sol of ferric hydroxide can be prepared by precipitating ferric chloride with potassium carbonate and dialyzing out the electrolytes. Sols which are dispersed by pure water can also be purified by precipitating them with a monovalent salt which is not strongly adsorbed, filtering off the supernatant liquid, and peptizing the sol with water. Odén used this method to purify his sulfur sols.

Stabilizing Agents.—Nearly all lyophilic colloid sols are stabilized by the presence of attached or strongly adsorbed ions. The mechanism of stabilization is electrical and the sols can be precipitated by electrolytes. Colloidal sols can also be stabilized by the adsorption of stable colloids. Colloids which are stabilized in this way are very resistant to precipitation by salts and have all the surface properties of the stabilizing agent. Their properties resemble the properties of stabilized emulsions.

There is of course no sharp dividing line between lyophilic and lyophobic colloids. Although we think of proteins as stable, hydrophilic colloids, many of them are unstable at the isoelectric point or can be precipitated by polyvalent ions. Likewise some mineral colloids are so stable that they can be dried and redispersed in water. Odén found sulfur sols with all degrees of stability between his hydrophilic sol produced from concentrated solutions of H_2S and SO_2, and the completely unstabilized sol obtained by pouring an alcoholic solution of sulfur into water.

In nonaqueous media, ionic stabilization is rare because very few electrolytes are soluble in these liquids. Some detergents are soluble in hydrocarbons, however, and pigment particles which are dispersed in xylene by organic sulfonate ions will move in an electrical field.[7] Oxidized transformer oils are electrically conducting and the conductivity can be simulated by dissolving organic bases and organic acids in the pure oil.[8] It is therefore not possible to rule out electrostatic repulsion as a stabilizing influence in nonaqueous sols.

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[6] See Weiser, H. B., *Colloid Chemistry*, p. 143 (1939).

[7] Damerell, V. R., Gayer, K., and Laudenslager, H., *J. Phys. Chem.* **49**, 436 (1945).

Sols in organic liquids may be stabilized by oil-soluble soaps, especially the soaps of polyvalent metals and sulfonic acids. Oil-soluble high polymers, such as rubber and some plastics, are good stabilizing agents in nonaqueous systems, as are some phospholipids and other organic phosphate esters. Comparatively little work has been done on the production of dilute organosols, whereas a great deal of work has been done on concentrated suspensions of mineral pigments in oil paints. Good stabilizing agents prevent the pigment particles from sticking together and flocculating. By keeping the particles dispersed, the stabilizing agent increases the covering power of the paint, reduces the rate of sedimentation, and makes it easier to remix the settled pigment.[9]

One measurement of the protective action of a stable colloid is the gold number. The gold number is defined as the number of milligrams of the protective colloid which, when added to 10 ml of a red gold sol prepared from formaldehyde and K_2CO_3, just fails to prevent the change from red to blue when 1.0 ml of 10% NaCl is added. The gold number depends upon the size of the gold particles, because smaller particles will be more numerous and have a greater surface area. Zsigmondy recommends that the sol be prepared by the nuclear method in such a way that it contains particles approximately 250 Å in diameter. The gold number is greater the finer the particles.

The gold number measures the protective action of a colloid at only one concentration and it is not closely related to any other property of the colloid. For example, the gold number is not a good indication of the wetting power, or the detergent power of a soap. It is, however, a fairly sensitive indicator of small amounts of strongly adsorbed impurities. For example, albumin has a relatively large gold number, whereas the other proteins with which it is associated in nature have small gold numbers. The purity of a preparation of albumin can therefore be tested by the gold number.

Some stable colloids have a precipitating action instead of a protecting action on lyophobic sols, such as the gold sol. In dilute solutions some proteins will change a red gold sol to blue, or may only sensitize it so that it is turned blue by a smaller quantity of salt. The same protein may have a protective action at higher concentrations. If there is sufficient protein to cover the gold particles completely, the sol will be stabilized by the protein. If there is insufficient protein to cover the particles of gold, the protein may stick several particles together and favor coagulation. The relative size of the particles will also influence the final result.

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[8] Gemant, A., *J. Chem. Phys.* **14**, 424 (1946).

[9] See Fisher, E. K., and Gans, D. M., *Alexander's Colloid Chemistry* **6**, 286 (1946).

The sensitizing proteins present in pathological spinal fluid are the basis of Lange's gold sol reaction. Normal spinal fluid diluted 1:10 or more with 0.4% NaCl does not change the color of an unprotected red gold sol. Some of the proteins which are present in certain neural disorders will precipitate or sensitize the sol at certain dilutions. This test has a purely empirical diagnostic value[10] and the active substances responsible for the reactions have not been identified. The colloidal gold reagent for Lange's test is difficult to prepare so that it will be sensitive enough and yet not too sensitive. Two alternative tests, using colloidal benzoin and colloidal mastic, have been proposed but they are not as sensitive as the gold reaction. The reagents are much easier to prepare since either mastic or benzoin can be dispersed as a colloidal sol by pouring an alcoholic solution into water.

When two suspensoid sols bearing oppositely charged ions are mixed, the mixture may coagulate completely or it may remain in suspension. For every pair of sols there will be a range of concentrations in which coagulation occurs. Outside of this zone all of the particles in the mixed sol will bear the same charge as one of the two original sols. There is little doubt that the sol particles of opposite charge are adsorbed on each other and the sol which is present in excess determines the charge of the composite particle. If the two sols are present in equivalent quantities the composite particles will bear insufficient ions for stability and will coagulate.

The ability of one sol to keep another sol in solution frequently causes serious analytical difficulties. For example, chromic oxide sols, which bear negative Cr—O$^-$ ions in alkaline solutions will keep in suspension colloidal oxides of Fe_2O_3, MnO, CoO or NiO.

Smokes and Fogs.—Smokes and fogs are dispersions of solid and liquid particles in a gaseous medium. They are frequently called aerosols.[11] The particles of smokes and fogs are rarely smaller than 1000 Å and may be as large as a few tenths of a millimeter. Many aerosols are completely unstabilized and persist in the air for a relatively short period of time.

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[10] See any good Clinical Laboratory Text, such as:

Kolmer, J. A., *Clinical Diagnosis by Laboratory Examination*, p. 343 (1943).

Todd, J. C., and Sanford, A. H., *Clinical Diagnosis by Laboratory Methods*, 10th Ed., p. 598 (1943).

See Weiser, H. B., *Colloid Chemistry*, p. 251 (1939).

A smoke will be destroyed if the particles settle out on the walls of the container. The rate of sedimentation is from 50 to 100 times the rate of sedimentation in aqueous systems for comparable density differences. Fog particles with a diameter of 2000 Å will settle at a rate of about 1 cm per hour; with a diameter of 0.2 mm at a rate of about 2.5 miles per hour. Very small particles may be kept aloft indefinitely by the stirring action of convection currents in the air.

Destruction of an aerosol by sedimentation is augmented by the coagulation of the primary particles to form secondary particles which sediment more rapidly. The particles of some aerosols are completely unstabilized and will stick together, if they come in contact. These aerosols coagulate fairly rapidly. Many particles adsorb one or more layers of air on their surfaces and the adsorbed layers keep the particles from sticking together unless they collide forcibly. The adsorbed layer of air behaves like a rather inefficient stabilizing colloid.

Aerosols may carry electrical charges but, unlike the conditions in aqueous systems, ions of opposite sign will combine as ion pairs or neutral particles. The kinetic energy of the ions is insufficient to cause dissociation, and a soluble counter-ion is unknown in gaseous systems. Ions in gases always have a transient existence. It is possible to charge all the particles of an aerosol with the same charge by passing the aerosol through a brush discharge of free electrons. An aerosol which contains particles all charged with the same sign is unstable because the like charges cause the particles to repel one another and the cloud expands until it is deposited on the walls of the container.

The Cottrell precipitator makes use of electrostatic attracting to remove mists and smokes from flue gases and other industrial processes. The gases are made to pass a series of points which are charged to a high potential. The sharp points give off electrons which become attached to the smoke and dust particles. These are then attracted to, and coagulate upon, an oppositely charged plate electrode. The deposited material frequently contains valuable constituents, such as As_2O_3 smoke from smelting operations, or dust high in potash content from cement plants.[12]

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[11] The name Aerosol is also a trade name for a series of wetting agents, see p. 223.

[12] See Welch, H. V., *Alexander's Colloid Chemistry* 6, 274 (1946).

The formation of aerosols requires either the presence of nuclei or a high degree of supersaturation. When air that is saturated with water vapor is expanded rapidly, it cools and becomes supersaturated. If the air is free from nuclei the supersaturation must exceed sevenfold before nuclei will form. At sevenfold supersaturation enough nuclei form to produce a fog; below this the few stray nuclei collect the excess water vapor and grow so large that they fall as rain.

The most effective nucleus for the condensation of water vapor is a gas ion. An ion attracts the water dipoles and forms a small nuclear drop. The potential on this drop is inversely proportional to the radius, and increasing the radius decreases the potential. The charge thus opposes the tendency of the molecules to evaporate and holds them in the drop making it stable. Surface tension forces exert large pressures on small drops and increase the vapor pressure of the drop. A small uncharged drop will therefore be unstable and will evaporate. The presence of a charge on the drop opposes this influence and stabilizes small drops against evaporation.

The C.T.R. Wilson cloud chamber makes use of the ability of ions to act as condensation nuclei for water drops. When a high velocity charged particle passes through air it produces a very large number of ion pairs along its track. The track can therefore be made visible by supersaturating the air with water vapor. The Wilson cloud chamber contains a close fitting cylinder or a rubber diaphragm which can be lowered rapidly to expand and supersaturate the air (or argon) which is initially saturated with water (or alcohol) vapor. The air must first be cleared of extraneous nuclei. This can be done most conveniently by forming a fog and then clearing it by applying a high potential to an electrode in the chamber.[13] Figure 12–1 shows a simple form of a Wilson cloud chamber for demonstration purposes. Figures 12–2a, b, and c show photographs of the tracks produced by different particles in a cloud chamber.

Drops of water can also be stabilized by the presence of a solute in the drop which lowers the vapor pressure. Molecules of SO_3 are very powerful nuclei, and SO_3 gas will pick up water vapor from moist air to produce a stable fog. This fog interferes with the absorption of SO_3 in water in a sulfuric acid plant. The SO_3 molecules pick up water to form a fog when SO_3 gas, mixed with air, is bubbled through water. The fog particles move much more slowly than molecules and therefore have a small chance of hitting the walls of

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[13] See Locher, G. L., *Rev. Sci. Inst.* 7, 471 (1936).

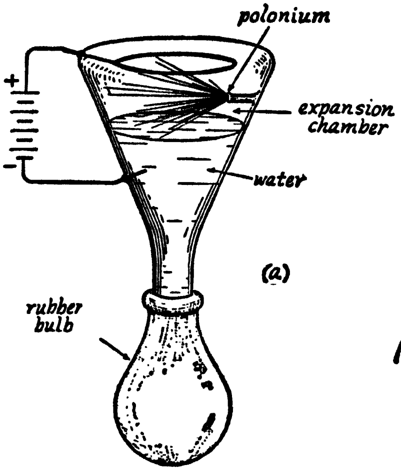

Fig. 12.1. Fog-track chamber.

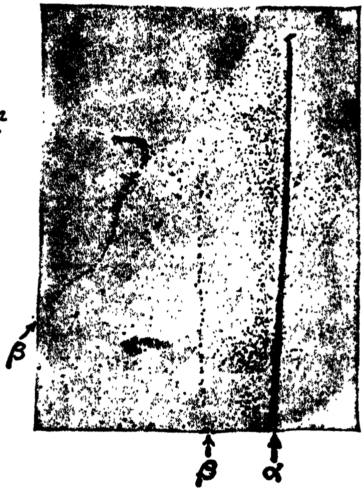

Fig. 12.2*a*. Rays of α and β particles.

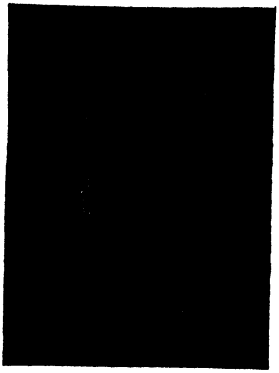

Fig. 12.2*b*. Fog-track of a transmutation.

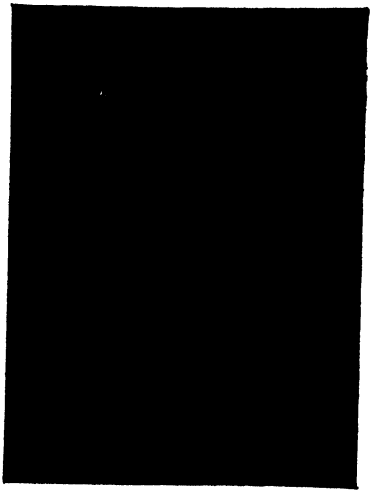

Fig. 12.2*c*. Fog-track of uranium fission.

the air bubbles. Most of them will be carried out into the air. This loss of SO_3 is avoided by absorbing the SO_3 in sulfuric acid which has a low enough pressure of water vapor to prevent the formation of a fog. The same trouble comes up if you try to remove SO_3 fumes from a Kjeldahl digestion by sucking the fumes into a water jet aspirator pump. The fog which is formed passes right through the pump and escapes into the air at the outlet of the pump. The fumes might be absorbed in a bottle of sulfuric acid which is fitted with a spray trap.

Stable fogs for screening purposes may be made by spraying oleum (concentrated sulfuric acid) into the air. Many metal halides hydrolize in the air to produce HCl and a hydrous oxide. For example,

$$SiCl_4 + 2\,H_2O \longrightarrow 4\,HCl + SiO_2.$$

These substances pick up water vapor from moist air to produce a fog. They are useless in dry air. Smokes for screening purposes are usually produced by heating a solid which is easily vaporized and will condense to form an opaque smoke. There have been many recent developments in the production of smokes for military purposes. Colored smokes for example are produced by volatilizing dyes; the color is due to the solid dye particles in the smoke.

Aerosol insecticide bombs contain an easily liquefiable propellent gas, such as CCl_2F_2 (Freon), which is nontoxic and, in the liquid state, is a good solvent for the insecticide (DDT). The bombs usually also contain an oil carrier for the insecticide. When the valve is opened the pressure of the propellent forces the contents out as a stream of small drops. The propellent evaporates leaving the insecticide in minute drops of the carrier oil. The oil helps to stick the insecticide to any solid object it meets, such as the body of an insect or the walls of the room. A stable protected aerosol which would remain in the air and not be deposited on surfaces would not be satisfactory for this application. Particles of DDT on the walls are effective contact insecticides for several months after application.

Aerosols sprayed from the mouth and nose when talking, coughing or sneezing may carry infective organisms which will survive for many hours. One method of sterilizing air containing infective aerosols is to spray it with propylene glycol. The glycol vapor is taken up by the aerosol so that the drops contain a large percentage of glycol in which the bacteria cannot live. Some smokes and incense are also bacteriocidal.[14]

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[14] See Jennison, M. W., *Alexander's Colloid Chemistry* **5**, 1099 (1944).

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QUESTIONS AND PROBLEMS FOR FURTHER STUDY

CHAPTER 1. INTRODUCTION

1. Make a list of five noncolloidal common substances. Make another list of ten which are colloidal. Make use of the index to this book to check your answers. Save your answers for revision when you finish this book.

2. Express the following dimensions in centimeters, microns and Ångstrom units. (*a*) 0.5461μ; (*b*) 3.1mμ; (*c*) 0.01 mm; (*d*) 20 Å; (*e*) 1.47 cm; (*f*) 1.54×10^{-8} cm; (*g*) 1000 Å; (*h*) 5×10^{6} Å.

3. Derive the ratio between surface area and volume for a very long rod.

4. Calculate the area in cm^2 of 1 gm of carbon black if the particles have a mean diameter of 45 Å and a density of 2.5.

5. Calculate the area in acres per pound of a charcoal which consists of 50% by volume of pores with a mean diameter of 15 A. (*Hint:* the inside surface of the pores is equal to the outside surface of the rods of air which fill them.)

6. One of the mica-like minerals occurs in plates which are 7.2 Å thick. How many grams would be necessary to cover one square kilometer?

7. A sample of MgO occurs as uniform cubes which are reported to have an area of 750 cm^2 per gm. The density is 3.65. Calculate the length of one side of these particles.

8. Calculate the fraction of the atoms of Mg and O which lie at the surface of the sample of Question 7. The distance between Mg and O is 2.1 Å.

9. Are all colloidal materials finely divided? Explain.

10. Give specific examples, other than those mentioned, for each of the 8 types of colloidal dispersions.

CHAPTER 2. METHODS OF MEASUREMENT

1. Describe two different measurements which can be made with an ultracentrifuge and point out similarities and differences in the information to be obtained from them.

2. List the different methods for determining the size of: (*a*) a gold sol; (*b*) a hydrated protein; (*c*) channel black carbon; (*d*) rubber molecules; (*e*) bacteria.

3. Do all colloids show the Tyndall effect? Explain.

4. In a radio murder story the weapon, a dagger of crown glass, was hidden in a glass jar of liquid. Make use of a handbook of chemistry or physics and tell what you can about the liquid.

5. Why is it impossible at present to see a *living* virus which has a diameter of 200 Å?

6. How could you detect a thin surface layer of Fe_2O_3 on a piece of partially oxidized iron covered with Fe_3O_4?

7. How would you detect the presence of molecules of a nonvolatile hydrocarbon in a channel black whose particles are essentially spheres 100 Å in diameter?

8. Can the ultracentrifuge be applied to the study of particles which are lighter than water? How is Stokes' law applied in this case?

9. Some of Faraday's gold sols made in 1857 were on the borderline of visibility in the ultramicroscope. How far could they have settled since then if there had been no convection currents in the container?

10. Design an apparatus for the removal of electrolytes from 100 ml of a suspension of methyl cellulose in water.

CHAPTER 3. SURFACES

1. If two neutral atoms in contact are attracted with a force of 10^{-6} dynes, what is the attractive force between these atoms when their centers are 3 diameters apart?

2. By what percentage is the repulsive force between two atoms increased when the distance between their centers is reduced by 1%?

3. Two ions of opposite charge in water attract each other with a force of 3×10^{-7} dynes when they are 10 Å apart. What is the attractive force between them when they are 20 Å apart?

4. Calculate the pressure inside a bubble 5μ in diameter in water.

5. Calculate the rise of benzene in a capillary 0.1 mm in diameter. Use a handbook for the necessary data.

6. One half ml of a benzene solution of an unknown organic acid was spread on water leaving a film which was compressed to an area of 200 cm². Assume that the organic acid was linear and packed to an area of 20.5 Å². Calculate the concentration of the acid in the benzene.

7. What would be the capillary rise or fall of water in a paraffin tube 0.5 mm in diameter if the contact angle is 105°?

8. Suggest some practical applications of cationic wetting agents; of anionic wetting agents.

9. A tri-glyceride occupies a space 4 Å by 15 Å on the base and 20 Å high. How many square meters will be covered by 1 gm of this material? By 1 mol?

CHAPTER 4. ADSORPTION

1. List three examples of sorption which you have encountered in the last week.

2. Name good sorbants for the following substances: (*a*) water vapor; (*b*) CCl_4; (*c*) the brown color in vinegar; (*d*) oxygen.

3. Contrast physical and chemical sorption on the same sorbant (but at different temperatures) with regard to the capacity of the sorbant at (*a*) high pressures; (*b*) very low pressures.

4. Why is it more efficient to adsorb dry cleaning fumes on charcoal than to dissolve them in a petroleum oil?

5. Why is it impractical to adsorb water insoluble vapors on the surface of water instead of on charcoal?

6. Calculate and graph adsorption isotherms from the following data for the sorption of color from variously diluted molasses samples. In each case 100 ml of solution was shaken with 1 gm of charcoal for 1 hr and the color of the filtrate was measured.

I		II	
Initial Color	*Final Color*	*Initial Color*	*Final Color*
100	90.0	100	9.5
50	40.5	80	3.4
30	21.3	60	1.4
20	11.7	50	0.95
15	7.75	40	0.65
10	3.35	20	0.24
5	0.24		
3	0.14		
2	0.00		

7. Plot the adsorption isotherms of Problem 7 on log-log paper.

8. How low a concentration of a dye could you get by filtering a solution of the dye through a column of active charcoal?

9. Which is a better drying agent, $CaCl_2$ or dry cotton wool (see also page 159)? Why not use dry cotton wool in drying tubes instead of $CaCl_2$? (See *Organic Syntheses Collective Volume* 2, Introduction.)

10. Draw on graph paper a Langmuir isotherm with $a = 3$ and $b = 1$. On the same graph draw the Freundlich isotherm with $k = 0.75$ and $n = 2$. Use the same x/m and P units for both curves.

11. Calculate the value of x/m for a monolayer of nitrogen adsorbed on a piece of mica 0.01 mm thick. Assume that the density of mica is 3.0 and the N_2 molecule occupies an area of 14 Å^2.

12. When methyl alcohol vapors are oxidized by air on a silver catalyst the products are formaldehyde and methylal, $CH_3OCH_2OCH_3$. Suggest a method for recovering the methylal and formaldehyde separately.

13. A dye has a thickness of 7 Å and a density of 1.43. Calculate the weight of dye which could be adsorbed by a gram of charcoal which had a surface area of 700 cm^2 per gm.

14. In the previous question, if the surface area had been measured with nitrogen, what error would probably be introduced into your calculations?

CHAPTER 5. IONIC ADSORPTION

1. Would lead be likely to co-precipitate with barium sulfate in the presence of excess barium ions?

2. A large flask is rinsed with methylene blue chloride and then with water until the dye is barely detectable in the wash water. The flask is then rinsed with a little 10% NaCl which becomes blue. After removal of the NaCl more dye is extracted from the flask with glacial acetic acid. Explain.

3. How could you best remove the excess sulfuric and acetic acid remaining in solution after acetylating a sugar?

4. A clay soil becomes more acid after treating with neutral KCl. Explain.

5. Suggest a practical method for recovering glucose from acid hydrolyzed wood waste.

6. Some waters are purified by the addition of alum which hydrolizes and enmeshes the bacteria in a slimy precipitate of aluminum hydroxide. This treatment may also soften the water. Why? (Refer to Chapter 11 if necessary.)

7. Devise a method for the determination of magnesium and sulfate on the same sample by making use of ion exchange resins.

8. Devise a method for the determination of sodium formate in dilute aqueous solutions of formaldehyde containing bicarbonate ions.

9. Make a list of the ways in which sorption aids or hinders the analytical chemist.

10. What qualitative relation would you predict between the sharpness of a chromatographic band and the constants of the Freundlich adsorption isotherm?

CHAPTER 6. HIGH POLYMERS

1. Name two properties of a high polymer which change as the chain length is increased and tell the direction of the change. Name two other properties which are nearly independent of chain length.

2. Explain specific cases in which the formation of links between colloidal particles would: (*a*) hasten sedimentation; (*b*) greatly retard sedimentation.

3. List the factors which increase adhesion between the chains of a high polymer. List other factors which decrease the adhesion.

4. What is the approximate length in microns of the Carbowax polymer mentioned at the bottom of page 113.

5. Account for the fact that a synthetic high polymer does not form macroscopic crystals.

6. Estimate the number-average molecular weight and the weight-average molecular weight of the polyisobutylene sample shown in Figure 6–2, page 115. Assume a sharp cut-off at 6500 carbon atoms. Each carbon atom in the chain contributes 28 molecular weight units.

7. Choose good solvents for each of the following substances: (*a*) sugar; (*b*) acetamide; (*c*) glucose pentaacetate; (*d*) acetophenone; (*e*) paraffin wax; (*f*) ice; (*g*) benzene hexachloride, $C_6H_6Cl_6$.

8. What would happen if water were added to a solution of rubber in hexane and acetone?

9. Does quicksand show dilatancy or plasticity (perhaps with thixotropy)?

10. Apply Archimedes' principle to quicksand, which is a suspension of sand in water. How far could a quiet human body sink if the effective density of the quicksand were 2?

11. A series of spheres of the same diameter but different weights are dropped into a Bingham plastic of unit density. Compare the rate of fall of the spheres in the plastic and in water.

12. Sketch a curve of osmotic activity (osmotic pressure divided by concentration) for a non-electrolyte such as sucrose and for polyethylene glycol with a molecular weight of 4000.

13. Many powdered materials, such as glues or desserts, are mixed with water in a volume ratio of three parts of powder to one part of water. The wet mixture occupies only 2 volumes. Explain.

CHAPTER 7. PLASTICS, RESINS AND RUBBERS

1. Write equations for the formation of polyvinyl acetate from limestone, coke, and water.

2. How would you make a colloidal solution of polystyrene?

3. Suggest a method for preparing a thermosetting resin which consists largely of polymethylmethacrylate. How would you get the other starting materials?

4. Why do denture molding powders made from acrylic resins shrink only slightly when cured, whereas the monomers shrink about 20% during polymerization?

5. Predict the properties of the product produced by the dehydration of 6 hydroxy hexanoic acid until 99.5% of the water had been removed. You should be able to predict qualitatively the color, odor, appearance, boiling point, solubility, molecular weight and viscosity of a 1% solution in a good solvent.

6. Estimate the viscosity of a 1% rubber cement in benzene if the weight average molecular weight is 30,000.

7. What advantages might be gained by incorporating fillers in phenolic plastics?

8. Recommend a method for repairing a cracked polystyrene cup.

9. What type of X-ray diffraction pattern would you expect from a stretched rubber band?

10. What effect would stretching have on the sorption of benzene vapors by rubber? Conversely, what effect would the sorption of a small amount of benzene have on the tension of a stretched rubber band (at constant length)?

11. Why are plastic windshields unsuitable for automobiles?

12. Suggest a substitute for sulfuric acid in melting point baths. (Glycerine is too hygroscopic and mineral oils are very inflammable when hot.)

CHAPTER 8. CARBOHYDRATES AND PROTEINS

1. How could methyl cellulose be converted to a water insoluble gel at room temperature?

2. Do you think alcohol could be used for beating paper pulp? Acetone? Benzene?

3. What objections would there be to fabrics made of spun polystyrene fibers?

4. Why has starch no melting point?

5. If a starch granule, 50μ in diameter, consisted of a single amylopectin molecule, what would its molecular weight be? Assume a density of 1.5 for the starch.

6. Uncooked starch suspensions in cold water are very fluid but after cooking even a 1% solution is extremely viscous. Explain in terms of molecules.

7. Suggest a possible solvent for Nylon and indicate the temperature at which it would be effective.

8. What kind of dye could be used to dye silk and leave lace (linen) trimming undyed? What kind would leave Nylon trimming undyed?

9. Outline the points of similarity between the vulcanization of rubber and the tanning of hide.

CHAPTER 9. COLLOIDAL IONS

1. Quartz powder is suspended in a 0.1% solution of gelatine in 0.1 N HCl. Toward which pole will the particles move in an electrophoresis cell?

2. A porous glass membrane is immersed in a 0.1% solution of egg albumin in 0.1 N NH_4OH. Which way will the solution move when electrodes are placed on opposite sides of the membrane?

3. Explain why an ionic gel, not at its isoelectric point, should swell more than a non-ionic gel when placed in water.

4. Solid sodium stearate consists of a wad of fine crystalline fibers. Give three ways in which this material might sorb water.

5. Egg albumin, with a molecular weight of 34,000, is a thin liquid in 5% solution whereas gelatine with a comparable molecular weight is a viscous liquid or a gel under the same conditions. Explain.

6. Point out three significant differences between a natural protein, such as plasma globulin, and a synthetic polypeptide made by polymerizing the amino acids obtained from the hydrolysis of plasma globulin.

7. Account for the fact that solid glycine has all the properties of an ionic crystal yet a solution of glycine in water does not conduct an electric current.

8. Suggest a method of producing milk powder that does not have a cooked taste.

9. A certain ferric oxide sol coagulated when the zeta potential was reduced to below 35 mv. (Ghosh 1929). Calculate the velocity of the particles at this potential in a field of 10 volts per cm.

10. One gram of the sodium salt of carboxymethyl cellulose, containing 0.01 gm of sodium ions, is dissolved in 100 ml of water and placed in a dialyzer sack in a large volume of 0.01 N NaCl. Calculate the concentration of chloride ions in the sack at equilibrium if the volume is held constant.

11. Calculate the membrane potential in Problem 12.

12. Assuming that the blood plasma consists of approximately 0.16 N NaCl and 4% serum albumin with an equivalent weight of 5000, calculate the concentration of NaCl which will be in equilibrium with blood plasma across a membrane permeable only to water and NaCl.

13. In what ways do colloidal electrolytes such as soaps differ from ionized colloids such as proteins? In what ways are they similar?

14. Would a colloidal soap solution show a Donnan effect if the pores of the membrane are slowly permeated by the soap ions?

15. Calculate the charge on a soap micelle in water if the individual particles have 10 excess negative ions and a radius of 25 Å.

16. Why would ultracentrifuge measurements on synthetic high polymers be less useful than measurements on the naturally occurring water-soluble proteins?

CHAPTER 10. EMULSIONS AND FOAMS

1. Describe two ways in which an aqueous soap solution can remove kerosene from cotton rags.

2. How could you make an emulsion of a hard wax which might be suitable for use as a shoe polish?

3. What factors contribute to the stability of an emulsion?

4. Polyethylene glycol is soluble in water and benzene, but not in saturated hydrocarbons. Would you expect it to stabilize an emulsion of water in benzene? Why?

5. Gelatine is used to stabilize an emulsion of styrene in water, 1 to 4 by volume. Estimate the lower limit of particles diameter if a 0.1% solution of gelatine is used.

6. Suggest a method for determining the oil content of a commercial mayonnaise.

7. What might be added to dry whole milk powder to make it disperse readily in water?

8. A certain synthetic rubber latex was produced which could not be coagulated by any available reagents. What other methods could be used to get out the rubber?

9. Do you think that suds on the surface of dish washing water help remove dirt from the dishes? If not, do they have any other function?

10. What mechanical advantages might there be in applying crude oil weed killer as an emulsion?

CHAPTER 11. HYDROUS OXIDES AND SILICATES

1. If an ore consisting of silicate minerals and lead sulfide is floated with a cationic wetting agent (such as lauryl ammonium chloride) which component would you expect to find in the foam?

2. Will "ferric hydroxide" in an acetate buffer be more apt to adsorb magnesium or sulfate ions?

3. Why is it impossible to resuspend ignited "ferric hydroxide" in water?

4. What would be the potential of a particle of "ferric hydroxide" which has been 99% neutralized if each sol particle carried only one positive charge? Consider the sol particles to be spheres and the density of the particles to be 4.0.

5. How would you prepare a stable ferric hydroxide sol which would not be precipitated by electrolytes?

6. Why is glass spoiled if it crystallizes or vitrifies?

7. What is the fundamental difference between glass and mineral soil colloids?

8. What treatment would you suggest to make a pond with a clay bottom over sand more permeable to water so that the water would drain away rapidly and not stand for mosquitoes to breed in?

CHAPTER 12. LYOPHOBIC COLLOIDS OR SUSPENSOIDS

1. LaMer and co-workers have recently found that very fine dispersions of sulfur in water show no crystallinity although the melting point of sulfur is 112° C. Explain.

2. Compare and contrast the methods for obtaining colloidal sols of sulfur and polystyrene.

3. Why is it impossible to have a pure stable mercury sol?

4. How would you make a stable mercury sol?

5. Would it be possible to make a stable sol of calcium sulfate in water? Why? In alcohol? How?

6. Suggest a rapid method for preparing a titania sol from an aqueous solution of $TiCl_4$.

7. Would it be possible to make a sol of iron metal? Under what conditions would it be stable?

8. Why do colloidal precipitates frequently fail to pass through filter paper?

9. When two similar colloids, one with a large gold number and the other with a small gold number are mixed, will the mixture have a large or a small gold number?

10. Why is cloth a better dust filter than granular charcoal?

11. Would you expect large or small particles of an insecticide to kill flies more rapidly in a given time, assuming that particles are always much smaller than the flies?

12. In sufficiently cold weather smokeless powder produces a fog when fired into the air. Why?

APPENDIX

SYMBOLS AND CONSTANTS

A	Area in cm^2.
a	Amplitude of a displacement in cm; a constant in the Langmuir isotherm.
b	A constant in the Langmuir isotherm.
β	*See* Greek letters at the end of this table.
C	A constant; concentration.
C_s	Concentration of a saturated solution.
c	A constant.
D	Diffusion coefficient in cm^2 per sec.
d	Diameter of a circle or sphere, side of a square or cube, in cm.
E	Potential in volts.
e	Charge on an electron, 4.80×10^{-10} absolute electrostatic units: base of natural logarithms.
F	Faraday's constant, 96,500 coulombs.
f	Frictional coefficient.
g	Acceleration of gravity. 980 cm/sec^2; osmotic coefficient.
h	Height in cm.
I	Current in amperes.
J	Force in dynes.
K	Dielectric constant.
k	Boltzman's constant, $R/N = 1.38 \times 10^{-16}$ erg/degree.
L	Conductivity.
l	Length in cm.
M	Membrane potential in volts.
m	Mass in grams.
N	Avogadro's number, the number of molecules in a gram mol, 6.02×10^{23}.
n	A number.
P	Pressure (absolute) in dynes per cm^2.
Q	Quantity of diffusing material.
R	Gas constant. 1.99 calories per mol degree, 8.31 erg per mol degree; symbol for an arbitrary organic radical.

r	Radius in centimeters; resolution in centimeters.
r.p.m.	Revolutions per minute.
S	Svedberg, 10^{-13} sec.
s	Sedimentation constant in sec^{-1}.
s_{20}	Sedimentation constant corrected to 20° C.
T	Absolute temperature, °C + 273.
t	Time (in seconds).
u	Mobility in cm per sec.
$\underline{V}$	Volume in cm^3.
$\bar{V}$	Partial specific volume.
v	Velocity in cm per sec.
W	Work in ergs.
x	Distance in cm; quantity of sorbed material as in x/m.
z	Valence of an ion.

Greek Letters

α (alpha)	Glucosidal link; keratin configuration.
β (beta)	Glucosidal link; keratin configuration.
γ (gamma)	Surface tension in dynes per cm.
ζ (zeta)	Zeta potential in volts.
η (eta)	Viscosity in poise.
η_0	Viscosity of solvent.
η_{sp}	Specific viscosity.
$[\eta]$	Intrinsic viscosity.
Θ (Theta)	Contact angle.
θ (theta)	Bragg angle.
λ (lambda)	Wave length in cm, equivalent mobility.
μ (mu)	Micron, 10^{-4} cm, ionic strength.
Π (Pi)	Osmotic pressure, usually in atmospheres.
π (pi)	3.14159 . . . .
ρ (rho)	Density in gm per cm^3.
σ (sigma)	Surface pressure in dynes per cm.
Φ (Phi)	Fraction of a surface which is covered in the derivation of the Langmuir isotherm.
ϕ (phi)	Angular aperture.
ω (omega)	Angular rotation in radians per second.

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